

AD-A132 236

SHOCK INDUCED MOLECULAR EXCITATION IN SOLIDS(U) NAVAL
SURFACE WEAPONS CENTER SILVER SPRING MD F J ZERILLI
06 APR 83 NSWC/TR-83-90 SBI-AD-F500 197

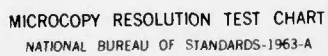
1/1

UNCLASSIFIED

F/G 20/8

NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

NSWC TR 83-90

ADA 132236

SHOCK INDUCED MOLECULAR EXCITATION IN SOLIDS

BY FRANK J. ZERILLI

RESEARCH AND TECHNOLOGY DEPARTMENT

6 APRIL 1983

Approved for public release, distribution unlimited.

DTIC
ELECTE
AUG 25 1983
S E D



NAVAL SURFACE WEAPONS CENTER

Dahlgren, Virginia 22448 • Silver Spring, Maryland 20910

DTIC FILE COPY

83 08 24 011

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NSWC TR 83-90	2. GOVT ACCESSION NO. ADA132 236	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) SHOCK INDUCED MOLECULAR EXCITATION IN SOLIDS		5. TYPE OF REPORT & PERIOD COVERED
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Frank J. Zerilli		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Surface Weapons Center (Code R13) White Oak Silver Spring, MD 20910		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F, 2301, A,R 13AB
11. CONTROLLING OFFICE NAME AND ADDRESS AFOSR/XOP Bolling AFB Washington, D.C. 20332		12. REPORT DATE 6 April 1983
		13. NUMBER OF PAGES 63
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Shock Waves	Nitromethane	Adiabatic Approximation
Molecular Excitation	Acoustic Modes	Born-Oppenheimer Approximation
Molecular Relaxation	Lattice Vibrations	Anharmonic Effects
Energy Transfer	Internal Modes	Non-Radiative Transitions
Condensed Matter	Molecular Vibrations	Pressure-Time Critical Relation
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
<p>Initiation of condensed explosives is studied on a molecular level with a quantum mechanical calculation of transition rates for shock induced transitions between low lying internal molecular normal mode states in a molecular solid. It is assumed that the shock produces a distribution of acoustic phonons which becomes thermalized before any significant internal mode phonons are created. The calculation uses the Born-Oppenheimer approximation in which the internal modes constitute the fast subsystem and the acoustic modes constitute the slow system. A sample calculation is done for nitromethane. Generally</p>		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

speaking, the lowest frequency internal modes have the fastest shock induced transition rates, with the transition from the ground to first excited state being the slowest. The transition rates increase by six to ten orders of magnitude from the values under normal conditions when nitromethane is subjected to shocks of 50 to 300 kbar. The transition lifetimes are compared with, and show some correlation with, the pressure-time critical shock initiation data obtained by de Longueville, Fauquignon, and Moulard.

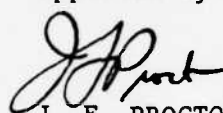
UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

FOREWORD

This work is an interim report on studies of a fundamental nature concerning the transfer of energy from shock waves into the internal modes of molecules in solid explosives and has application to the study of initiation and shock sensitivity of explosives. The work is supported principally by Air Force Office of Scientific Research Project/Task 2301/A6, AFOSR-MIPR-82-00004.

Approved by:



J. F. PROCTOR, Head
Energetic Materials Division

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	



PREFACE

I wish to thank Dr. Edward T. Toton, formerly of NSWC, who began this work and introduced me to this subject and who has since provided me with many stimulating discussions. Thanks are also due to Drs. R. D. Bardo, C. S. Coffey, S. J. Jacobs, H. D. Jones, and D. J. Pastine for many useful discussions. Appreciation is expressed to Connie M. Cronin for typing the manuscript.

CONTENTS

<u>Chapter</u>		<u>Page</u>
1	INTRODUCTION	1
	OBJECTIVE	1
	HISTORY	1
	CHARACTERIZATION OF THE SHOCK	2
	ACOUSTIC MODES THERMALIZE ON PICOSECOND TIME SCALE.	2
	BORN-OPPENHEIMER APPROXIMATION APPLICABLE TO INTERNAL MODES . .	3
	NON-ADIABATIC OPERATOR INDUCES NON-RADIATIVE INTERNAL MODE TRANSITIONS	3
	AN APPROXIMATE EXPRESSION FOR THE NON-RADIATIVE TRANSITION RATE.	4
	CHARACTERISTICS OF THE NON-RADIATIVE TRANSITION RATE.	4
	INTERPRETATION OF THE STOKES PARAMETER.	5
2	THEORY	6
	USE BORN-OPPENHEIMER APPROXIMATION.	6
	GOLDEN RULE TRANSITION RATE EXPRESSION.	6
	CONDON APPROXIMATION.	7
	INTEGRAL EXPRESSION FOR THE TRANSITION RATE	8
	APPROXIMATE EVALUATION OF THE TRANSITION RATE INTEGRAL.	9
3	MODEL HAMILTONIAN AND BORN-OPPENHEIMER SOLUTION	10
	MOLECULAR LATTICE HAMILTONIAN	10
	BORN-OPPENHEIMER SEPARATION	12
	INTERNAL MODE (FAST SUBSYSTEM) SOLUTION	13
	EQUILIBRIUM ACOUSTIC NORMAL COORDINATES	14
	NON-ADIABATIC OPERATOR MATRIX ELEMENTS.	14
	ESTIMATING NORMAL MODE ANHARMONIC COUPLING COEFFICIENTS	14
4	RADIATIVE TRANSITIONS AND THE STOKES SHIFT	17
	GOLDEN RULE FOR RADIATIVE TRANSITIONS	17
	HUANG-RHYS FACTOR RELATED TO MOMENTS OF SPECTRAL DISTRIBUTION.	17
	SPECTRAL BAND SHAPE NOT GAUSSIAN.	18
	HOW TO DETERMINE HUANG-RHYS FACTOR.	18
	SADDLE POINT APPROXIMATION NOT GOOD FOR RADIATIVE TRANSITIONS	18

CONTENTS (Cont.)

<u>Chapter</u>		<u>Page</u>
5	APPLICATION TO NITROMETHANE	19
	LIQUID VERSUS CRYSTALLINE NITROMETHANE.	19
	PARAMETERS TO BE DETERMINED	19
	HUANG-RHYS FACTORS FOR NITROMETHANE	19
	TRANSITION RATES VERSUS DEBYE FREQUENCY AND TEMPERATURE	21
	RELATION OF DEBYE FREQUENCY TO COMPRESSION.	23
	TRANSITION RATES ALONG HUGONIOT	23
	PRESSURE-TIME CRITICAL RELATION	23
	COMPARISON WITH PRESSURE-TIME CRITICAL INITIATION DATA	26
6	CONCLUSION	29
<u>Appendix</u>		<u>Page</u>
A	BORN-OPPENHEIMER APPROXIMATION	A-1
B	NON-ADIABATIC OPERATOR	B-1
C	EVALUATION OF SUM OVER STATES	C-1
D	SADDLE POINT INTEGRAL FOR TRANSITION RATE	D-1
E	EVALUATION OF L_{kfi} and m_{kfi}	E-1
F	ACOUSTIC MODE WAVE EQUATION APPROXIMATE SOLUTIONS	F-1
G	APPROXIMATE TRANSITION RATE FORMULA	G-1
H	MOMENTS OF SPECTRAL BAND SHAPE FUNCTION	H-1
I	DETERMINATION OF STOKES PARAMETER FROM BANDWIDTH	I-1
J	VALIDITY OF THE SADDLE POINT APPROXIMATION	J-1

ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	TRANSITION RATES FOR SEVERAL INTERNAL MODES OF NITROMETHANE VERSUS DEBYE FREQUENCY	22
2	DEBYE FREQUENCY OF NITROMETHANE AS A FUNCTION OF PRESSURE ALONG THREE SHOCK HUGONIOT'S WITH INITIAL TEMPERATURES OF 244°K, 298°K, AND 373°K	24
3	DATA SHOWN IN FIGURE 2 BUT ON A LOG-LOG SCALE	25
4	NON-RADIATIVE (SHOCK-INDUCED) TRANSITION RATES FOR SEVERAL INTERNAL MODES OF NITROMETHANE PLOTTED AS A FUNCTION OF SHOCK PRESSURE ALONG THE HUGONIOT WITH INITIAL TEMPERATURE 298.2°K	27
5	DATA OF FIGURE 4 BUT ON A LOG-LOG SCALE	28

TABLES

<u>Table</u>		<u>Page</u>
1	HUANG-RHYS PARAMETER FOR SOME OPTICALLY ACTIVE INTERNAL MODES OF NITROMETHANE (CH ₃ NO ₂)	20

CHAPTER 1

INTRODUCTION

OBJECTIVE

This is an interim report on work which, it is hoped, will lead to a greater understanding of how the energy from a shock wave is transferred to the internal vibrational modes of molecules in solid explosives. Thus, the work should be applicable to the study of the initiation and shock sensitivity of explosives. If we could, for example, predict shock induced energy transfer rates for particular types of bonds, then we could design energetic materials with preferred initiation and sensitivity characteristics.

HISTORY

In 1979, D. J. Pastine and co-workers pointed out that because many explosives have weak intermolecular bonds and strong covalent intramolecular bonds the average frequency of intramolecular vibrations (internal mode or optical mode vibrations), ω_o , would be much higher than the average frequency of intermolecular (lattice mode or acoustic mode) vibrations, ω_a , with the ratio ω_o/ω_a typically of the order of ten.¹ Thus, the immediate effect of a shock on such materials would be to increase the temperature of the acoustic vibrational branch while leaving the optical branches at the initial temperature. The relaxation time required before the internal molecular temperature reaches a critical value sufficient for the shock to grow to detonation would be sufficiently long so as to be comparable to and indeed determine the shock pulse duration required to produce detonation at a given shock pressure. In other words, the relaxation time for thermal equilibration of the internal modes is the controlling factor in the initiation of reactions. Using a simple classical mass and spring model, Pastine et al. estimated that, at a shock temperature of 500°K, the lower limit to the acoustic/optical relaxation time is of the order of several microseconds for systems in which the acoustic frequencies ω_a are around 10^{13} rad/sec and the optical mode frequencies ω_o are around 10^{14} rad/sec. They

¹Pastine, D. J., Edwards, D. J., Jones, H. D., Richmond, C. T., and Kim, K., "Some New Concepts Relating to the Initiation and Failure of Detonable Explosives," in High Pressure Science and Technology, Vol. 2, ed by K. D. Timmerhaus and M. S. Barber, Plenum, New York, 1979.

also predicted that the relaxation times would be very sensitive functions of the frequency ratio ω_o/ω_a with the relaxation times decreasing by four orders of magnitude when the ratio decreases from 10 to 6. Thus, the very lowest frequency intramolecular modes, which are typically bending rather than stretching modes, should be the most important in the relaxation process.

The work of Pastine, et al., was followed by that of E. T. Toton who developed a more refined quantum mechanical description which exploited the disparity between intra- and inter-molecular mode vibrational frequencies.* The results of Toton's calculations also pointed toward the importance of the lowest frequency intramolecular modes in the relaxation process. In this work, we will develop Toton's model, calculate shock induced internal mode transition rates for nitromethane, and attempt to relate our results to critical shock initiation data for nitromethane.

CHARACTERIZATION OF THE SHOCK

When a shock wave travels through a solid material, it excites the lattice normal vibrational modes to higher levels or, in other words, creates acoustic phonons. The shock also compresses the solid, increasing the frequency of the acoustic modes. We wish to calculate the rate at which acoustic mode energy is transferred to the molecular internal modes (relaxation rate). For this purpose, it is assumed that the distribution of acoustic mode energy relaxes to a thermal distribution in a time which is short compared to the time required to create a significant number of optical (internal mode) phonons. Thus, one immediate effect of the shock is to raise the temperature of the acoustic modes while leaving the internal modes "cold." The non-radiative transition rates between internal mode levels then give an estimate of the rate at which the internal modes relax to the new, higher temperature. Later, we will need to determine the change in the average acoustic mode frequency produced by the shock. This can be deduced approximately from the compression by integrating the Grüneisen parameter along the shock Hugoniot. Hence, in this model, the effect of the shock can be characterized by two quantities, the compression and the acoustic mode temperature produced by the shock.

ACOUSTIC MODES THERMALIZE ON A PICOSECOND TIME SCALE

The assumption of rapid thermalization of the acoustic modes compared to the internal modes is not unreasonable since internal mode frequencies are generally much higher than lattice mode frequencies and this mismatch should greatly reduce the rate of energy transfer between lattice and internal modes. From the work of Van Vleck, we can estimate that the acoustic modes should thermalize on a picosecond time scale.² Van Vleck computed the rate of energy transfer between lattice oscillators due to anharmonic perturbations when different portions of the frequency spectrum are not in thermal equilibrium.

*Toton, E. T., NSWC/WO, unpublished.

²Van Vleck, J. H., "Calculation of Energy Exchange between Lattice Oscillators," Physical Review, 59, 730 (1941).

His result for the transition rate from level n to level $n-1$ for a particular lattice oscillator when the temperature of the main body of lattice oscillations is at a temperature T is

$$W_{n \rightarrow n-1} \sim n D (T/T_D)^2 v_D^5 \quad (1)$$

where v_D is the Debye frequency, T_D is the Debye temperature, and D is a constant characteristic of the solid. The value of D is about 10^{-51} sec^4 for typical solids. Equation (1) is valid for $T > T_D$. For $n=1$, $T=300^\circ\text{K}$, and $v_D \approx 3 \times 10^{12} \text{ Hz}$, Equation (1) gives transition lifetimes of the order of 10^{-12} seconds.

BORN-OPPENHEIMER APPROXIMATION APPLICABLE TO INTERNAL MODES

Van Vleck used the usual first order perturbation theory to calculate the transition rate. While this is satisfactory in the case of lattice relaxation, it will prove unsatisfactory, in most cases, for lattice-internal mode relaxation since internal mode frequencies may be an order of magnitude greater than lattice mode frequencies. An exchange of energy between lattice and internal modes which creates, for example, one optical phonon will involve the annihilation of five, ten, or more acoustic phonons. To determine the transition rate in this case would require a fifth, tenth, or greater order perturbation calculation. Thus, Toton* developed a Born-Oppenheimer formalism analogous to the adiabatic approximation used in treating the coupling of localized electronic states to lattice vibrations³ and similar to a formalism described by Lin.⁴ In this formalism, the lattice modes are considered the slow subsystem components and the internal modes are considered the fast subsystem components. The approximation gets better as the disparity between internal and lattice frequencies increases.

NON-ADIABATIC OPERATOR INDUCES NON-RADIATIVE INTERNAL MODE TRANSITIONS

In the Born-Oppenheimer approximation, the total Hamiltonian H of the system is separated into two parts, the adiabatic part \mathcal{H} and the non-adiabatic part \mathcal{L} . The Born-Oppenheimer states are eigen-solutions of \mathcal{H} . The non-adiabatic part \mathcal{L} can be considered an interaction which induces non-radiative transitions between the stationary Born-Oppenheimer states.

*Toton, E. T., NSWC, unpublished.

³Perlin, Yu. E., "Modern Methods in the Theory of Many-Phonon Processes," Soviet Physics-Uspekhi, 6, 542 (1963).

⁴Lin, S. H., "Theory of Vibrational Relaxation and Infrared Absorption in Condensed Media," J. Chem. Phys., 65, 1053 (1976).

AN APPROXIMATE EXPRESSION FOR THE NON-RADIATIVE TRANSITION RATE

In order to obtain an expression for the non-radiative transition rate between internal mode levels, we expand the interatomic potential in a series of terms up to the third order in the vibrational normal coordinates. The order of magnitude of the third order coefficients is obtained from dimensional arguments to be described later. In addition, we make an approximation of the Condon type in which we assume that certain internal mode matrix elements do not depend on acoustic mode coordinates. We also assume that the acoustic modes can be characterized by a single average frequency which we will refer to as the Debye frequency. Then, isolating a single internal mode and ignoring the interaction between internal modes, we obtain (from the non-adiabatic operator) the following rate for a transition from internal mode level n to level $n+1$.

$$W_{n \rightarrow n+1} = (n+1) \frac{(2n+1)[2n+1+(2n+5)\omega_D/\omega_o] + 4\omega_D^2/\omega_o^2}{1 + 5\omega_D/\omega_o + 4\omega_D^2/\omega_o^2} W_{01} \quad (2)$$

$$W_{01} = 4\sqrt{2\pi} (1 + 5\omega_D/\omega_o + 4\omega_D^2/\omega_o^2) \Delta\Omega \sqrt{\frac{\omega_o}{\omega_D}} \left(\frac{T}{T^*}\right)^{\omega_o/\omega_D} e^{-\hbar\omega_o/2kT} \quad (2a)$$

$$T^* = \frac{\hbar\omega_o}{ke} \frac{2\omega_D}{\Delta\Omega} \quad (2b)$$

In Equation (2a), T is the temperature of the thermalized acoustic modes, ω_o is the circular frequency of the internal mode, and ω_D is the (circular) Debye frequency. The anharmonic coupling effects are all condensed into the quantity $\Delta\Omega$, called the Stokes shift. Equations (2), (2a), (2b) are valid for temperatures T greater than the Debye temperature T_D ($=\hbar\omega_D/k$, k is Boltzmann's constant) but less than $T_D\omega_D/\Delta\Omega$. We will see later that $\omega_D/\Delta\Omega \gg 1$. For the Born-Oppenheimer approximation to be valid, it is required that $\omega_o/\omega_D \gg 1$. To obtain the transition rate $W_{n \rightarrow n-1}$, change the sign of the argument of the exponential function in Equation (2a) and change $n+1$ to n in the first factor in Equation (2).

CHARACTERISTICS OF THE NON-RADIATIVE TRANSITION RATE

Several inferences may be made from Equation (2) and (2a). For transitions between low lying levels, transitions between the ground and first excited states will have the longest lifetimes. The internal modes with the lowest frequencies ω_o generally will have the greatest non-radiative transition rates due to the factor

$$(T/T^*)^{\omega_o/\omega_D}.$$

This factor also can lead to large increases in transition rate for relatively small increases in temperature and Debye frequency.

INTERPRETATION OF THE STOKES PARAMETER

The Stokes parameter $\Delta\Omega$ which appears in Equation (2a) has a simple interpretation for optically active internal modes. The coupling between internal and lattice modes splits a single internal mode absorption or emission line into a band of lines and the maximum for the emission band is lower in frequency than the maximum for the absorption band by an amount $\Delta\Omega$. In addition, the second moment of the band is a function of $\Delta\Omega$.⁵ If the band shape were gaussian, there then would be a straightforward relation to the band width. This is the case when the formalism is applied to electronic states (F-centers in alkali halides). However, as we will see, the band shape for internal vibrational modes is highly non-gaussian so that it is difficult to extract $\Delta\Omega$ from the band width.

In the next chapter we discuss the formal development of the theory.

⁵Lax, M. J., J. Chem. Phys., 20, 1752 (1952).

CHAPTER 2

THEORY

USE BORN-OPPENHEIMER APPROXIMATION

We apply the Born-Oppenheimer approximation to the normal vibrational modes of a molecular lattice. The internal modes constitute the fast subsystem and the acoustic modes constitute the slow subsystem. The separation of the total Hamiltonian into an adiabatic part \mathcal{H} and a non-adiabatic part \mathcal{L} which induces non-radiative transitions between Born-Oppenheimer states is described in Appendix A.

GOLDEN RULE TRANSITION RATE EXPRESSION

Let n_k be the acoustic mode quantum number for a mode of frequency ω_k . Let i be an internal mode quantum number for an initial internal mode state and let f be the quantum number for the final internal mode state. Let n denote the set of initial acoustic mode quantum numbers $\{n_k\}$ and let m denote the set of final acoustic mode quantum numbers $\{m_k\}$. Then the transition rate from the initial to final state produced by the non-adiabatic interaction is obtained from first order time-dependent perturbation theory (golden rule).

$$W(i, n \rightarrow f, m) = \frac{2\pi}{\hbar} |\langle f, m | \mathcal{L} | i, n \rangle|^2 \delta(E_{fm} - E_{in}) \quad (3)$$

We are interested in the total transition rate assuming a thermalized distribution of acoustic mode levels, so we must sum Equation (3) over final acoustic states m and average it over initial acoustic states n . The result is

$$W(i \rightarrow f) = \frac{2\pi}{\hbar} \sum_{m, n} P_n |\langle f, m | \mathcal{L} | i, n \rangle|^2 \delta(E_{fm} - E_{in}) \quad (4)$$

where P_n is the probability that an acoustic state with quantum numbers $\{n_k\}$ is realized. For a thermalized distribution, this is a Boltzmann probability distribution.

$$P_n = Q^{-1} e^{-\beta E_n} \quad (5a)$$

$$Q = \sum_n e^{-\beta E_n} \quad (5b)$$

$$\beta = 1/kT \quad (5c)$$

$$E_n = \sum_{\kappa} (n_{\kappa} + \frac{1}{2}) \hbar \omega_{\kappa} \quad (5d)$$

The validity of using the golden rule, Equation (3), for the transition rate has been studied by Lin using a master equation approach.⁶

CONDON APPROXIMATION

The remainder of this discussion will be concerned with evaluating the transition rate given by Equation (4). When the slow subsystem is a collection of harmonic oscillators the form of the non-adiabatic operator \mathcal{L} is given in Appendix B, Equation (B-2). Using this expression, we obtain the matrix element

$$\langle f_m | \mathcal{L} | i_n \rangle = - \sum_{\kappa} \hbar \omega_{\kappa} \left\{ \langle \psi_f \phi_{f_m} | \frac{\partial \psi_i}{\partial q_{\kappa}} \frac{\partial \phi_{i_n}}{\partial q_{\kappa}} \rangle + \frac{1}{2} \langle \psi_f \phi_{f_m} | \frac{\partial^2 \psi_i}{\partial q_{\kappa}^2} \phi_{i_n} \rangle \right\} \quad (6)$$

If we assume that the reduced matrix elements

$$\mathcal{L}_{\kappa fi} = - \hbar \omega_{\kappa} \langle \psi_f | \frac{\partial \psi_i}{\partial q_{\kappa}} \rangle \quad (7a)$$

$$\mathcal{M}_{\kappa fi} = - \frac{1}{2} \hbar \omega_{\kappa} \langle \psi_f | \frac{\partial^2 \psi_i}{\partial q_{\kappa}^2} \rangle \quad (7b)$$

do not depend on the acoustic coordinates q_{κ} (our "Condon approximation"), then we may write

$$\langle f_m | \mathcal{L} | i_n \rangle = \sum_{\kappa} \left\{ \mathcal{L}_{\kappa fi} \langle \phi_{f_m} | \frac{\partial \phi_{i_n}}{\partial q_{\kappa}} \rangle + \mathcal{M}_{\kappa fi} \langle \phi_{f_m} | \phi_{i_n} \rangle \right\} \quad (8)$$

While the Condon approximation is often a good one in dealing with electronic states, its validity is more questionable in this case. However, the simplification it produces is considerable. Similarly, it is often assumed that the $\mathcal{M}_{\kappa fi}$ term in Equation (8) can be neglected compared to the $\mathcal{L}_{\kappa fi}$ term since the $\mathcal{M}_{\kappa fi}$ term contains the second derivative of the wave function with respect to the slow system coordinates. Because of the questionable validity of this assumption and because dropping the term leads to no appreciable simplification, we will retain it.

⁶Lin, S. H., "On the Master Equation Approach of Vibrational Relaxation in Condensed Media," J. Chem. Phys., 61, 3810 (1974).

INTEGRAL EXPRESSION FOR THE TRANSITION RATE

The sum appearing in Equation (4) can be converted to an integral by several methods summarized by Perlin in his review article (See Reference 3, footnote p. 3). One convenient method involving the use of the integral representation of the delta function is outlined in Appendix C. The resulting transition rate (see Equation (C-9)) is

$$W(i \rightarrow f) = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} F_{fi}(t) \exp \left\{ i\omega_{fi} t + \sum_{\kappa} F_{\kappa}(t) \Delta_{\kappa fi}^2 - S \right\} dt \quad (9)$$

where

$$\begin{aligned} F_{fi}(t) = & \sum_{\kappa} |\mathcal{L}_{\kappa fi}|^2 F_{\kappa}(t) + \sum_{\kappa} \mathcal{L}_{\kappa fi} \Delta_{\kappa fi} E_{\kappa}(t) \sum_{\lambda} \mathcal{L}_{\lambda fi}^* \Delta_{\lambda fi} E_{\lambda}(t) \\ & + \sum_{\kappa, \lambda} (m_{\kappa fi}^* \mathcal{L}_{\lambda fi} + m_{\kappa fi} \mathcal{L}_{\lambda fi}^*) \Delta_{\lambda fi} E_{\lambda}(t) \\ & + \left| \sum_{\kappa} m_{\kappa fi} \right|^2 \end{aligned} \quad (9a)$$

$$F_{\kappa}(t) = \frac{\cosh(i\omega_{\kappa} t + \frac{1}{2} \beta \hbar \omega_{\kappa})}{2 \sinh(\frac{1}{2} \beta \hbar \omega_{\kappa})} \quad (9b)$$

$$E_{\kappa}(t) = F_{\kappa}(t) - \frac{1}{2} \coth(\frac{1}{2} \beta \hbar \omega_{\kappa}) \quad (9c)$$

$$S = \sum_{\kappa} \frac{1}{2} \coth(\frac{1}{2} \beta \hbar \omega_{\kappa}) \Delta_{\kappa fi}^2 \quad (9d)$$

$$\Delta_{\kappa fi} = q_{\kappa f} - q_{\kappa i} \quad (9e)$$

In Equation (9e), $q_{\kappa f}$ and $q_{\kappa i}$ are the equilibrium values of the dimensionless acoustic normal coordinate q_{κ} when the internal mode is in states f and i , respectively.* We define our dimensionless coordinates to be those which put the kinetic energy operator in the form shown in Equation (B-1) in Appendix B.

*See Appendix F.

APPROXIMATE EVALUATION OF THE TRANSITION RATE INTEGRAL

An approximate evaluation of the integral in Equation (9) may be obtained by the method of steepest descents as described by Perlin (Reference 3, footnote, p. 3) and outlined in Appendix D. The result is still somewhat unweildy so we make the further approximation that the sums over the acoustic modes can be replaced by sums in which the frequencies ω_k are replaced by some average frequency ω_D . For convenience, we will refer to ω_D as the Debye frequency although the connection is somewhat tenuous. However, there is some evidence that the average frequency determined from the lattice infrared absorption spectrum correlates well with the Debye frequency determined by other methods, for example, from specific heat data.⁷

The transition rate expression resulting from these approximations is reproduced below.

$$W(i \rightarrow f) = \frac{1}{\hbar^2} \sqrt{\frac{2\pi}{g''(z_0)}} F_{fi}(-iz_0) \exp\{g(z_0)\} \quad (10)$$

where

$$g''(z_0) = \omega_D^2 P \quad (10a)$$

$$\exp\{g(z_0)\} = \exp\left\{\frac{1}{2} \beta \hbar \omega_D P + P - S\right\} \left\{\frac{x}{|P| + P}\right\}^{|P|} \quad (10b)$$

$$\begin{aligned} F_{fi}(-iz_0) = & \sum_k |\mathcal{L}_{kfi}|^2 F_D + \left| \sum_k \mathcal{L}_{kfi} \Delta_{kfi} \right|^2 \left\{ F_D - S/2S_0 \right\}^2 \\ & + 2 \operatorname{Re} \left\{ \sum_k m_{kfi} \sum_\lambda \mathcal{L}_{\lambda fi} \Delta_{\lambda fi} \right\} \left\{ F_D - S/2S_0 \right\} \\ & + \left| \sum_k m_{kfi} \right|^2 \end{aligned} \quad (10c)$$

$$S = S_0 \coth\left(\frac{1}{2} \beta \hbar \omega_D\right) \quad (10d)$$

$$P = \sqrt{x^2 + p^2} \quad (10e)$$

$$F_D = P/2S_0 \quad (10f)$$

⁷Plendl, J. N., "New Spectral and Atomistic Relations in Physics and Chemistry of Solids," in Optical Properties of Solids, S. Nudelman and S. S. Mitra, eds., Plenum, New York (1969), p. 310 ff.

The three parameters p , S_0 , and x , appearing in the transition rate expression are defined below, Equations (11a-c).

$$p = - \frac{\omega_{fi}}{\omega_D} \quad (11a)$$

$$S_0 = \frac{1}{2} \sum_{\kappa} \Delta_{\kappa fi}^2 \quad (11b)$$

$$x = \frac{S_0}{\sinh\left(\frac{1}{2} \beta \hbar \omega_D\right)} \quad (11c)$$

The dimensionless quantity S_0 , introduced by Huang and Rhys,⁸ is a measure of the strength of the anharmonic coupling between a given internal mode and the acoustic modes. As we will see in Chapter 4, S_0 is a dimensionless Stokes shift, $S_0 = \Delta\Omega/2\omega_D$.

It remains to evaluate the internal mode reduced matrix elements, $\mathcal{L}_{\kappa fi}$ and $\mathcal{M}_{\kappa fi}$. For this, we need a specific model Hamiltonian to be described in the next chapter.

⁸Huang, K. and Rhys, A., "Theory of Light Absorption and Non-Radiative Transitions in F-Centers," Proc. Roy. Soc., A204, 406 (1950).

CHAPTER 3

MODEL HAMILTONIAN AND BORN-OPPENHEIMER SOLUTION

MOLECULAR LATTICE HAMILTONIAN

We write the Hamiltonian of a molecular lattice in the following form:

$$H = \sum_{n=1}^{3rN} \frac{1}{2} M_n \dot{u}_n^2 + V(u_1, \dots, u_{3rN}) \quad (12)$$

where u_n is the n 'th cartesian coordinate displacement from equilibrium, N is the total number of molecules, r is the number of atoms per molecule, and M_n is the mass of the atom associated with the n 'th coordinate. The potential energy V is a function of all the displacements. If we develop V in a power series we obtain

$$V = \sum_{m,n} V_{mn}^{(2)} u_m u_n + \sum_{l,m,n} V_{lmn}^{(3)} u_l u_m u_n + \dots \quad (13)$$

There is no linear term in Equation (13) since the u_n are displacements from equilibrium. Concentrating on the quadratic term in Equation (13), we may find a transformation to real, dimensionless normal coordinates in the form

$$u_n = \sum_{j=1}^{3rN} A_{nj} \sqrt{\frac{\hbar}{M_n \omega_j}} q_j \quad (14)$$

where A_{nj} is a real, orthogonal matrix. In the new coordinates, the Hamiltonian operator becomes

$$H = \sum_j \frac{1}{2} \hbar \omega_j \left(q_j^2 - \frac{\partial^2}{\partial q_j^2} \right) + \sum_{i,j,k} A_{ijk} q_i q_j q_k + \dots \quad (15)$$

where

$$A_{ijk} = \sum_{l,m,n} A_{li} A_{mj} A_{nk} V_{lmn}^{(3)} \sqrt{\frac{\hbar^3}{M_l M_m M_n \omega_l \omega_j \omega_k}} \quad (16)$$

Up to this point, we have made no distinction between lattice and internal modes. Now, following Toton,* we isolate one internal mode whose coordinate we designate q_0 . Greek subscripts will designate acoustic mode coordinates. Then, the Hamiltonian may be written in the following form:

$$H = \frac{1}{2} \hbar \omega_0 \left(q_0^2 - \frac{\partial^2}{\partial q_0^2} \right) + \sum_{\kappa} \frac{1}{2} \hbar \omega_{\kappa} \left(q_{\kappa}^2 - \frac{\partial^2}{\partial q_{\kappa}^2} \right) + q_0 \sum_{\kappa, \lambda} B_{\kappa \lambda} q_{\kappa} q_{\lambda} + q_0^2 \sum_{\kappa} C_{\kappa} q_{\kappa} + \dots \quad (17)$$

Since we are interested in the interaction between the internal mode q_0 and the acoustic modes q_{κ} , we have ignored terms which involve interactions with internal modes other than q_0 and anharmonic terms which involve internal modes alone or acoustic modes alone.

BORN-OPPENHEIMER SEPARATION

Following the Born-Oppenheimer prescription, we separate the Hamiltonian, Equation (17), into the fast part

$$H_0 = \frac{1}{2} \hbar \omega_0 \left\{ - \frac{\partial^2}{\partial q_0^2} + (1+2C) q_0^2 + 2Bq_0 + 2A \right\} \quad (18)$$

where

$$\begin{aligned} \hbar \omega_0 A &= \sum_{\kappa} \frac{1}{2} \hbar \omega_{\kappa} q_{\kappa}^2 \\ \hbar \omega_0 B &= \sum_{\kappa, \lambda} B_{\kappa \lambda} q_{\kappa} q_{\lambda} \\ \hbar \omega_0 C &= \sum_{\kappa} C_{\kappa} q_{\kappa} \end{aligned}$$

and the slow part

$$H_1 = - \sum_{\kappa} \frac{1}{2} \hbar \omega_{\kappa} \frac{\partial^2}{\partial q_{\kappa}^2} \quad (19)$$

*Toton, E. T., NSWC, unpublished.

The Born-Oppenheimer basis functions, therefore, are products

$$\Psi(q_0, q_K) = \psi(q_0, q_K) \phi(q_K) \quad (20)$$

where the first factor is a solution of the fast part

$$H_0 \psi_s = \epsilon_s(q_K) \psi_s \quad (21)$$

and the second factor is a solution of

$$\left\{ - \sum_K \frac{1}{2} \hbar \omega_K \frac{\partial^2}{\partial q_K^2} + \epsilon_s(q_K) \right\} \phi_{sn} = E_{sn} \phi_{sn} \quad (22)$$

The internal mode quantum number is s and the collection of acoustic mode quantum numbers is represented by n .

INTERNAL MODE (FAST SUBSYSTEM) SOLUTION

Equation (21) is a harmonic oscillator equation which we can reduce to standard form by making the change of variable

$$Z = \rho(q_0 - \bar{q}_0) \quad (23)$$

where

$$\rho^4 = 1 + 2C \quad (23a)$$

$$\bar{q}_0 = -\rho^{-4}B \quad (23b)$$

Then, Equation (21) becomes

$$\left\{ - \frac{1}{2} \hbar \omega_0 \rho^2 \left(\frac{\partial^2}{\partial Z^2} - Z^2 \right) + \frac{1}{2} \hbar \omega_0 \left(2A - \rho^{-4}B^2 \right) \right\} \psi_s = \epsilon_s \psi_s \quad (24)$$

with energy eigenvalues

$$\epsilon_s(q_K) = (s + \frac{1}{2}) \hbar \omega_0 \rho^2 + \left(A - \frac{1}{2} \rho^{-4}B^2 \right) \hbar \omega_0 \quad (25)$$

$$(s = 0, 1, 2, \dots)$$

The wave functions are

$$\psi_s(q_0, q_K) = \sqrt{\rho} \psi_s^{(HO)}(Z) \quad (26)$$

where $\psi_s^{(HO)}(z)$ is a normalized harmonic oscillator eigenfunction. The factor $\sqrt{\rho}$ normalizes the wave function as a function of q_0 . Both the energy eigenvalues and the wave functions depend parametrically on the acoustic coordinates q_k through the quantities A , B , and ρ .

EQUILIBRIUM ACOUSTIC NORMAL COORDINATES

The equilibrium acoustic normal coordinates are determined by the energy eigenvalues, Equation (25), which act as effective potentials for the acoustic wave equation. The equilibrium coordinates are derived in Appendix F and the result [Equation (F-3)] is

$$q_{ks} \cong -\left(s + \frac{1}{2}\right) \frac{C_k}{\hbar\omega_k} \quad (27)$$

where q_{ks} is the equilibrium value of coordinate q_k when the internal mode is in state s .

NON-ADIABATIC OPERATOR MATRIX ELEMENTS

We may substitute the wave functions, Equation (26), into Equations (7a,b) to obtain the non-adiabatic operator reduced matrix elements \mathcal{L}_{kfi} and \mathcal{M}_{kfi} . The calculation is outlined in Appendix E and the results are given in Equations (E-6) and (E-7). The matrix elements are functions of the acoustic coordinates, but, in the spirit of the Condon approximation, we will assume that they are constants with values obtained by substituting the equilibrium values of the acoustic coordinates for the internal mode in the initial state i . In addition, we assume that the third order anharmonic corrections to the Hamiltonian, Equation (17), are small so that the quantities $B, C \ll 1$ and $\rho \approx 1$.

The results of Appendix E indicate that the non-radiative transition rates are non-zero only for nearest-neighbor ($i \pm 1$) and next-nearest-neighbor ($i \pm 2$) transitions. Of these, the nearest neighbor transition rates will be typically larger by many orders of magnitude. Thus, from Equations (E-6, E-7) we obtain

$$\mathcal{L}_{k,i+1,i} = \frac{\omega_k}{\omega_0} \sqrt{2(i+1)} \left\{ \sum_{\lambda} B_{k\lambda} q_{\lambda i} - \frac{C_k}{\hbar\omega_0} \sum_{k,\lambda} B_{k\lambda} q_{ki} q_{\lambda i} \right\} \quad (28)$$

$$\mathcal{M}_{k,i+1,i} = \frac{\omega_k}{\omega_0} \sqrt{2(i+1)} B_{kk} \quad (29)$$

ESTIMATING NORMAL MODE ANHARMONIC COUPLING COEFFICIENTS

We are now in a position to determine the non-radiative transition rate if we estimate the normal mode anharmonic coupling coefficients $B_{k\lambda}$ and C_k .

Comparing Equations (16) and (17), we can obtain expressions for C_k and $B_{k\lambda}$ in terms of the third order coefficients of the power series development of the potential energy of the crystal. In particular, we write C_k and $B_{k\lambda}$ in the following suggestive forms

$$C_k = \frac{1}{\sqrt{N}} \frac{V_{3k}}{M^{3/2}} \frac{\hbar^{3/2}}{\omega_0 \sqrt{\omega_k}} \quad (30)$$

where

$$\frac{V_{3k}}{\sqrt{N} M^{3/2}} = \sum_{l,m,n} \frac{A_{l0} A_{m0} A_{nk}}{\sqrt{M_l M_m M_n}} v_{lmn}^{(3)} \quad (30a)$$

$$B_{k\lambda} = \frac{1}{\sqrt{N}} \frac{V_{3k\lambda}}{M^{3/2}} \frac{\hbar^{3/2}}{\sqrt{\omega_0 \omega_k \omega_\lambda}} \quad (31)$$

where

$$\frac{V_{3k\lambda}}{\sqrt{N} M^{3/2}} = \sum_{l,m,n} \frac{A_{l0} A_{mk} A_{n\lambda}}{\sqrt{M_l M_m M_n}} v_{lmn}^{(3)} \quad (31a)$$

In Equations (30a) and (31a), M is the mass of a molecule and N is the number of molecules. Since binding forces are not long range, the coefficients $v_{lmn}^{(3)}$ are significant only when l, m, n are nearly equal. Therefore, the triple sum has effectively the order of N terms. The orthogonal transformation coefficients A_{lj} are typically sinusoidal and proportional to $N^{-1/2}$. Therefore, C_k is proportional to $N \cdot N^{-3/2} = N^{-1/2}$. Apparently, this is true also of $B_{k\lambda}$ but it is not clear that there are not other constraints which determine the non-zero values of $B_{k\lambda}$. It is clear, for example, that the energy eigenvalues in Equation (25) should be essentially independent of the size of the system and so the quantity B appearing in Equation (25) and defined after Equation (18) should be essentially independent of N when B is evaluated for q_k equal to the equilibrium values q_{ks} . For this to be true, we require $B_{k\lambda}$ to be proportional to N^{-1} . Then Equations (30a) and (31a) define average third order coefficients V_{3k} and $V_{3k\lambda}$.

Calculations for a linear diatomic chain indicate that, for a rough approximation, we may set $V_{3k\lambda} \sim f'''(r_e)$ and $V_{3k} \sim 2^{-3/2} f'''(r_e)$ where $f(r)$ is a pair potential describing the intermolecular force and r_e is the equilibrium molecular separation. Using this approximation, we may obtain an estimate of the function F_{fi} which appears in the transition rate expression (see Equation (10c)). The calculation is described in Appendix G. When $S_0 \ll 1$ and $T_D < T < T_D/2S_0$, the resulting transition rate reduces to the expression in Equations (2, 2a, 2b) in which we have set $\Delta\Omega = \omega_D S_0/2$. The results of Appendix G (see Equation G-9) are combined with the transition rate expressions (Equations (10), (11)) and summarized below [Equations (32-32f)].

$$W_{i \rightarrow f} = \sqrt{2\pi} \omega_D \frac{1}{\sqrt{P}} \exp \left\{ g(z_0) \right\} \frac{F_{fi}}{(\hbar\omega_D)^2} \quad (32)$$

$$\exp \left\{ g(z_0) \right\} = \exp \left\{ \frac{1}{2} \frac{\hbar\omega_D}{kT} p + P-S \right\} \left\{ \frac{x}{|p|+P} \right\}^{|p|} \quad (32a)$$

$$\begin{aligned} \frac{F_{fi}}{(\hbar\omega_D)^2} = 8 \frac{S_0}{|p|} \left[(i+1)\delta_{f,i+1} + i\delta_{f,i-1} \right] \left\{ (2i+1)^2(P-S)^2 \right. \\ \left. + 4(2i+1)(P-S) + (2i+1)^2 P+4 \right\} \end{aligned} \quad (32b)$$

$$p = - \frac{\omega_{fi}}{\omega_D} \quad (32c)$$

$$x = S_0 / \sinh \left(\frac{1}{2} \beta \hbar \omega_D \right) \quad (32d)$$

$$P = \sqrt{p^2 + x^2} \quad (32e)$$

$$S = S_0 \coth \left(\frac{1}{2} \beta \hbar \omega_D \right) \quad (32f)$$

For up-transitions, the final state $f = i+1$ so that $\omega_{fi} = \omega_0$ where ω_0 is the internal mode vibrational frequency. For down transitions, $f = i-1$ so that $\omega_{fi} = -\omega_0$.

CHAPTER 4

RADIATIVE TRANSITIONS AND THE STOKES SHIFT

GOLDEN RULE FOR RADIATIVE TRANSITIONS

In order to obtain the transition rates for radiative transitions, we can adapt the formalism for non-radiative transitions by replacing the non-adiabatic operator \mathcal{L} by the dipole moment operator μ . The expression for the radiative transition rate corresponding to Equation (4) is then

$$W_{i \rightarrow f}(\pm\omega) = \frac{2\pi}{\hbar} \rho \sum_{m,n} P_n |\langle f, m | \mu | i, n \rangle|^2 \delta(E_{fm} - E_{in} \pm \hbar\omega) \quad (33)$$

where ρ is a factor involving the intensity of incident radiation (absorption) or density of radiation field states (emission) whose structure is not important for our discussion. The absorbed or emitted photon has frequency ω with the positive sign for emission and the negative sign for absorption. If we make use of the Condon approximation, we can assume that μ_{fi} ($= \langle f | \mu | i \rangle$) is a constant so that the radiative transition rate can be obtained from the last term in the non-radiative transition rate expression by replacing $|\sum_k m_{kfi}|^2$ with $\rho |\mu_{fi}|^2$ (see Appendix C, Equations (C-4)(C-9)). The result is that the emission or absorption at frequency ω is proportional to the integral

$$I(\pm\omega) = \int_{-\infty}^{\infty} e^{\pm i\omega t} + g(it) dt \quad (34)$$

where g is the function defined in Appendix D, Equation (D-2).

HUANG-RHYS FACTOR RELATED TO MOMENTS OF SPECTRAL DISTRIBUTION

It was first pointed out by Lax that the Huang-Rhys factor is directly related to the moments of the distribution, Equation (34) (see Reference 4, footnote p. 3). The derivation is repeated in Appendix H wherein it is shown that the Stokes parameter $\Delta\Omega$ is the difference between the means of absorption and emission bands and that $\Delta\Omega = 2S_0\omega_D$. It is also seen that the second moment is related to S_0 (Equation (H-13)):

$$\sigma^2 = \omega_D^2 S_0 \coth\left(\frac{1}{2} \beta \hbar \omega_D\right) \quad (35)$$

If the distribution were gaussian, it would be possible to determine S_0 by measuring the full width at half maximum, $\Delta\omega$, since, in this case,

$$\Delta\omega = 2\sqrt{2 \ln 2} \sigma \quad (36)$$

SPECTRAL BAND SHAPE NOT GAUSSIAN

Unfortunately, we see by examining the expressions for skewness and kurtosis (Equations (H-14)(H-15)) that the deviation from a gaussian distribution is considerable if $S_0 \ll 1$ which is the case for internal mode vibrations. Typical internal mode frequencies lie in the range 500 cm^{-1} to 2500 cm^{-1} (10^{14} sec^{-1} to $5 \times 10^{14} \text{ sec}^{-1}$) with typical infrared absorption bandwidths of $10\text{-}50 \text{ cm}^{-1}$. Typical Debye frequencies are around 100 cm^{-1} ($2 \times 10^{13} \text{ sec}^{-1}$ or 150°K). Thus, $\Delta\omega/\omega_D \sim 0.2$ which implies, from Equation (35), that $S \sim 1/200$ and, therefore, if $T > 75^\circ\text{K}$, that $S_0 < 1/200$. This is in sharp contrast to the situation for electronic transitions in F-centers where $\Delta\omega \sim 2000\text{-}5000 \text{ cm}^{-1}$ so that $S_0 \sim 20$ (see Reference 8, footnote, p. 10).

HOW TO DETERMINE HUANG-RHYS FACTOR

It is practically impossible to determine experimentally the moments of a typical infrared spectral band due to the presence of noise. Besides the mean frequency, the width at half maximum is about the only parameter which can be measured with any degree of accuracy. However, it is possible to relate the band width and the Stokes parameter even for a non-gaussian distribution using the method described in Appendix I. A band shape function with arbitrary third and fourth moments is chosen and the moments are constrained to satisfy Equations (H-13) - (H-15). Then S_0 can be determined from the bandwidth by finding the root of a transcendental equation. In the next chapter we will apply this procedure to the energetic material nitromethane.

SADDLE POINT APPROXIMATION NOT GOOD FOR RADIATIVE TRANSITIONS

By using the method of moments, we have not found it necessary to actually evaluate the integral in Equation (34). This is fortunate since the saddle point approximation which we used for the non-radiative transition rates is not a good one for the radiative rates. This point is discussed in Appendix J.

CHAPTER 5

APPLICATION TO NITROMETHANE

LIQUID VERSUS CRYSTALLINE NITROMETHANE

In this section, we apply the results of the preceding sections to the extensively studied and relatively simple condensed explosive material, nitromethane. One caveat is necessary, however. Under normal conditions, nitromethane is a liquid and even under the extreme conditions characteristic of detonations it most likely retains the structure of a liquid.* The preceding results apply, strictly speaking, to a material which has long range periodic structure. It is not clear what the absence of such a structure would have on the predicted transition rates. In order to make a direct comparison with the results to be presented, it will be necessary to perform shock experiments on solid nitromethane.

PARAMETERS TO BE DETERMINED

In order to apply the transition rate formula (Equation (32)), we need four parameters for a material. Two are characteristic of the state of the shocked material: the Debye frequency ω_D and the temperature T . Two are characteristic of the internal mode whose transition rate is to be determined: the vibration frequency ω_0 and the Huang-Rhys parameter S_0 .

The Debye frequency is a function of compression which, in turn, is directly related to the shock pressure via the Hugoniot relation. The internal mode vibrational frequencies are only slightly affected by compression** so that we can safely assume them to be constant.

HUANG-RHYS FACTORS FOR NITROMETHANE

The variation of the Huang-Rhys factor S_0 with compression is not known, but the bandwidths of infrared absorption bands generally increase slightly with compression. In the absence of more definitive data at the present time we will assume S_0 is constant. Table 1 lists values of several optically active internal modes of nitromethane. The values are calculated from the bandwidths

*See Reference 10, footnote p. 23.

**Typically less than 0.02% per kilobar for the optically active internal modes of nitromethane.

using the method described in Appendix I. Two values of S_0 are given, corresponding to the two slightly different representations of the band shape, Equations (I-5) and (I-6).

We should note here that the optically active modes are a subset of the tiny fraction of modes which have zero wave number out of the total of approximately Avogadro's number of internal modes.

TABLE 1. HUANG-RHYS PARAMETER FOR SOME OPTICALLY ACTIVE INTERNAL MODES OF NITROMETHANE (CH_3NO_2)

MODE	$\omega_0(\text{cm}^{-1})$	$\Delta\omega(\text{cm}^{-1})^*$	$S_0(\text{Eq. I-5})$	$S_0(\text{Eq. I-6})$
CH_3 rocking parallel to NO_2 plane	1104	29 ± 6	1.47×10^{-2}	1.39×10^{-2}
C-N stretch	923	6.5 ± 1.1	1.01×10^{-3}	9.6×10^{-4}
NO_2 symmetric bending	663	19 ± 2.3	7.3×10^{-3}	6.9×10^{-3}
NO_2 rocking perp. to NO_2 plane	609	8.2 ± 1.1	1.58×10^{-3}	1.50×10^{-3}
NO_2 rocking parallel to NO_2 plane	485	7.6 ± 1.5	1.37×10^{-3}	1.30×10^{-3}

*Bandwidths were measured from infrared absorption spectra obtained in a diamond-anvil cell at room temperature (295°K) and pressures of the order of 5-18 kbar. Spectra obtained by J. W. Brasch, Jr. of NSWC.

The data from which S_0 is calculated were obtained in a diamond anvil cell at room temperature (295°K) and relatively low pressures (5 to 18 kbar) by J. W. Brasch of NSWC. The nitromethane is in a solid polycrystalline form under these conditions.

The values calculated for S_0 are for a Debye frequency of 2×10^{13} rad/sec (106.2 cm^{-1} or 152.7°K). It was determined that this is a reasonable value for the Debye frequency at standard temperature and pressure by taking the centroid of the low frequency part of the infrared absorption spectrum of nitromethane.

TRANSITION RATES VERSUS DEBYE FREQUENCY AND TEMPERATURE

In Figure 1, we have plotted the transition rates given by Equation (32) for the internal modes listed in Table 1 using the values of S_0 given in the next to last column of the Table. The transition rate is plotted as a function of ω_D for 300°K (solid curves) and for 2100°K (dashed curves). The most noticeable feature of the curves is the large variation in transition rates with relatively small changes in ω_0 , ω_D , and T . The C-N stretching mode, with a frequency of $1.74 \times 10^{14} \text{ sec}^{-1}$ has a ground to first excited state transition rate of about $10^{-17} \text{ sec}^{-1}$ at a temperature of 300°K and ω_D of $2 \times 10^{13} \text{ sec}^{-1}$ (this point is beyond the scale of the graph). On the other hand, the NO₂ symmetric bending mode with about two thirds the C-N stretching frequency, three times the C-N stretch bandwidth, at seven times higher temperature and two times higher Debye frequency has a transition rate of 10^9 sec^{-1} , twenty six orders of magnitude greater.

One conclusion to be drawn from Figure 1 is that energy is initially coupled most rapidly into the lowest frequency internal mode, NO₂ rocking parallel to the NO₂ plane at 485 cm^{-1} . This is not to say that there are not other internal modes into which energy is coupled more rapidly since we presently have no transition rate information. We are discounting the NO₂ symmetric bending mode since the calculated large transition rate is due to its large apparent bandwidth and the band may actually be the superposition of two individual bands.

Another conclusion to be drawn from Figure 1 is that small increases in temperature and compression (compression increases the Debye frequency) will lead to large increases in the rate of energy transfer. We also note that the relative importance of the internal modes in energy relaxation can change with changes in temperature and compression. For example, at 300°K, the CH₃ rocking parallel to plane the NO₂ (CH₃ rock ||) has a significantly lower excitation rate than the NO₂ rocking perpendicular to the NO₂ plane (NO₂ rock ⊥), while at 2100°K the excitation rates are comparable, with the CH₃ rock || rate exceeding the NO₂ rock ⊥ at the higher values of ω_D .

Inserting numerical values in Equation (2), we discover that W_{12} is typically ten times greater than W_{01} , and W_{23} is typically forty times greater. Thus, the relaxation time for energy distribution among the low lying internal levels is determined by the ground to first excited state transition rate, W_{01} . We cannot say anything about transitions between levels lying near the top of the potential well since our analysis assumes a harmonic internal mode potential. At this point we can only say that, if the transitions between levels close to dissociation are also rapid, then the rate W_{01} would be the significant parameter determining the overall dissociation rate. We may expect energy to be redistributed between internal modes more rapidly than it would be transferred between acoustic and internal modes. Thus, the overall internal mode thermal relaxation time as well as the overall dissociation rate should be controlled by W_{01} for the fastest internal mode (which seems to be the NO₂ rock || in nitromethane).

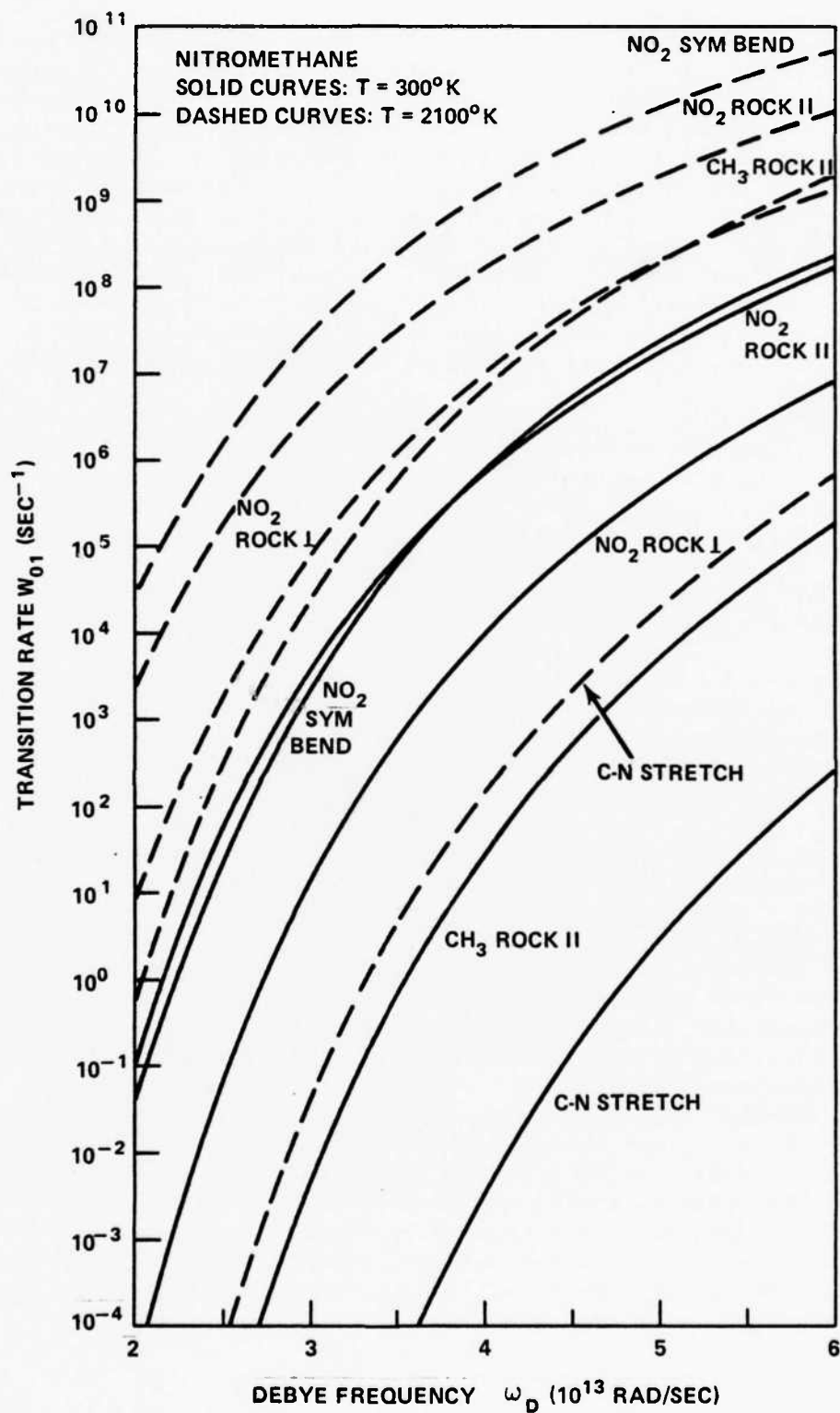


FIGURE 1. TRANSITION RATES FOR SEVERAL INTERNAL MODES OF NITROMETHANE VERSUS DEBYE FREQUENCY

RELATION OF DEBYE FREQUENCY TO COMPRESSION

Since we have repeatedly stressed (pun intended) the relation of Debye frequency to compression, it will be of interest to find this relation for nitromethane. We can determine this relation approximately by using the expression for the Grüneisen parameter which arises in the Debye mode of a solid,

$$\gamma = - \frac{d \ln \omega_D}{d \ln v} \quad (37)$$

where γ is the Grüneisen parameter and v is the specific volume.⁹ Integrating Equation (37) we get

$$\frac{\omega_D}{\omega_{D_0}} = \exp \left\{ - \int_{\ln v_0}^{\ln v} \gamma \, d \ln v \right\} \quad (38)$$

Hardesty and Lysne¹⁰ have calculated the thermodynamic properties of shocked nitromethane along Hugoniot's for initial pressure of 1 bar and initial temperatures of 244°K, 298°K, and 373°K. If we numerically integrate their Grüneisen parameter data according to Equation (38), we obtain the results shown in Figure 2. It is assumed that $\omega_{D_0} = 2 \times 10^{13} \text{ sec}^{-1}$. Figure 3 displays a log-log plot of the same data as Figure 2. From Figure 3 we see that, above 5 kbar, the curves are nearly linear indicating an approximate power law relation. The dashed lines are isotherms showing the shock temperature on each Hugoniot.

TRANSITION RATES ALONG HUGONIOT

Using the result shown in Figures 2 and 3 we can plot the transition rates versus pressure along a Hugoniot. This is done in Figure 4 for the Hugoniot with initial temperature 298°K. Again, Figure 5 is a log-log plot of the same data showing very close to power law curves above 5 kbar.

PRESSURE-TIME CRITICAL RELATION

If we disregard the NO₂ symmetric bending mode, the NO₂ rocking mode parallel to the NO₂ plane is the mode whose transition rate is the most important in energy transfer from the acoustic modes. If the transition rates calculated from Equation (32) are approximately correct and if the transition rate for the NO₂ rocking (parallel) mode is the controlling factor in the overall dissociation chain, then the plot of transition rate versus shock

⁹Born, M. and Huang, K., Dynamical Theory of Crystal Lattices, (Oxford Univ. Press, 1954), sec. 4.

¹⁰Hardesty, D. R. and Lysne, P. C., Shock Initiation and Detonation Properties of Homogeneous Explosives, Sandia Laboratories Report SLA 74-0165, May 1974.

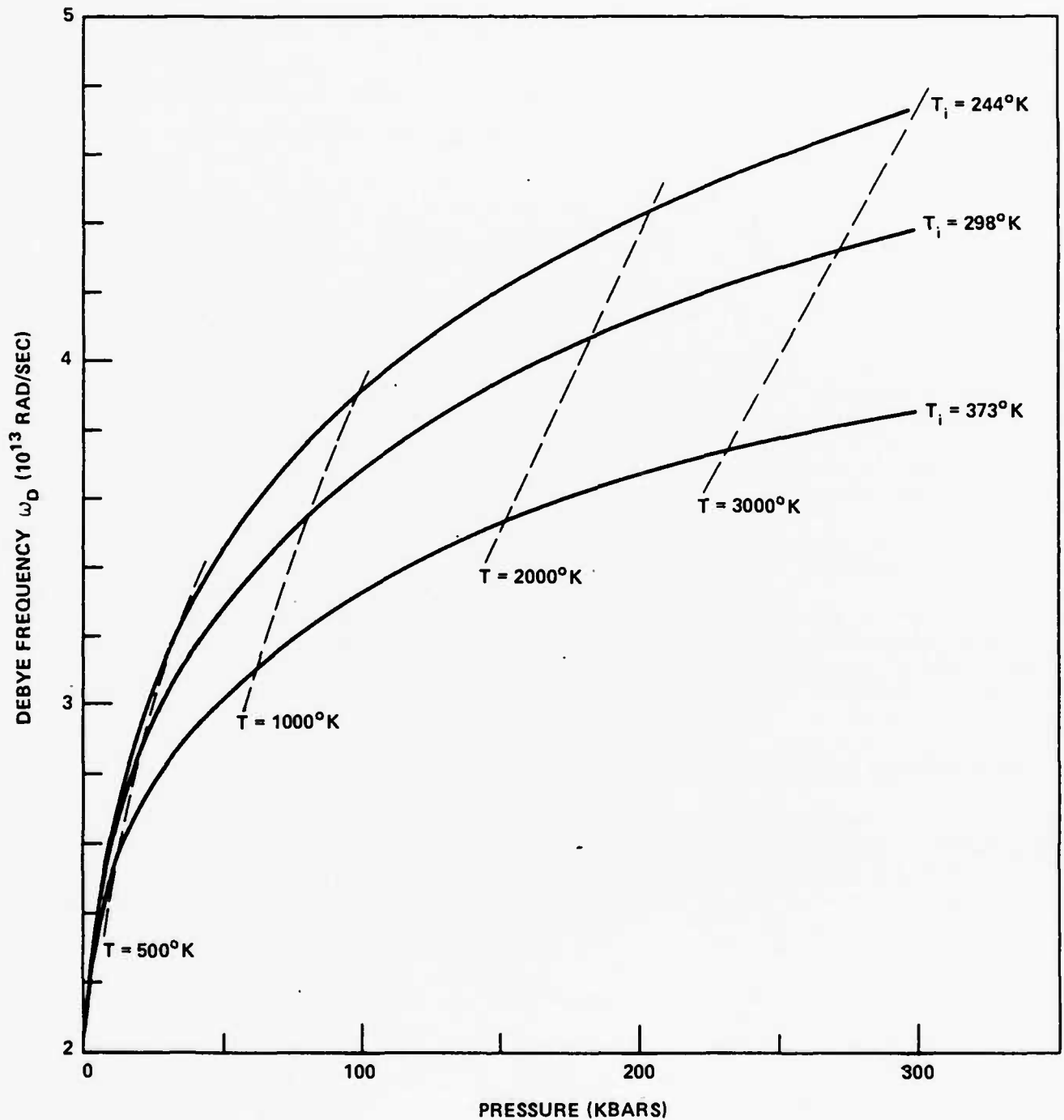


FIGURE 2. DEBYE FREQUENCY OF NITROMETHANE AS A FUNCTION OF PRESSURE ALONG THREE SHOCK HUGONIOTS WITH INITIAL TEMPERATURES OF 244°K , 298°K , AND 373°K

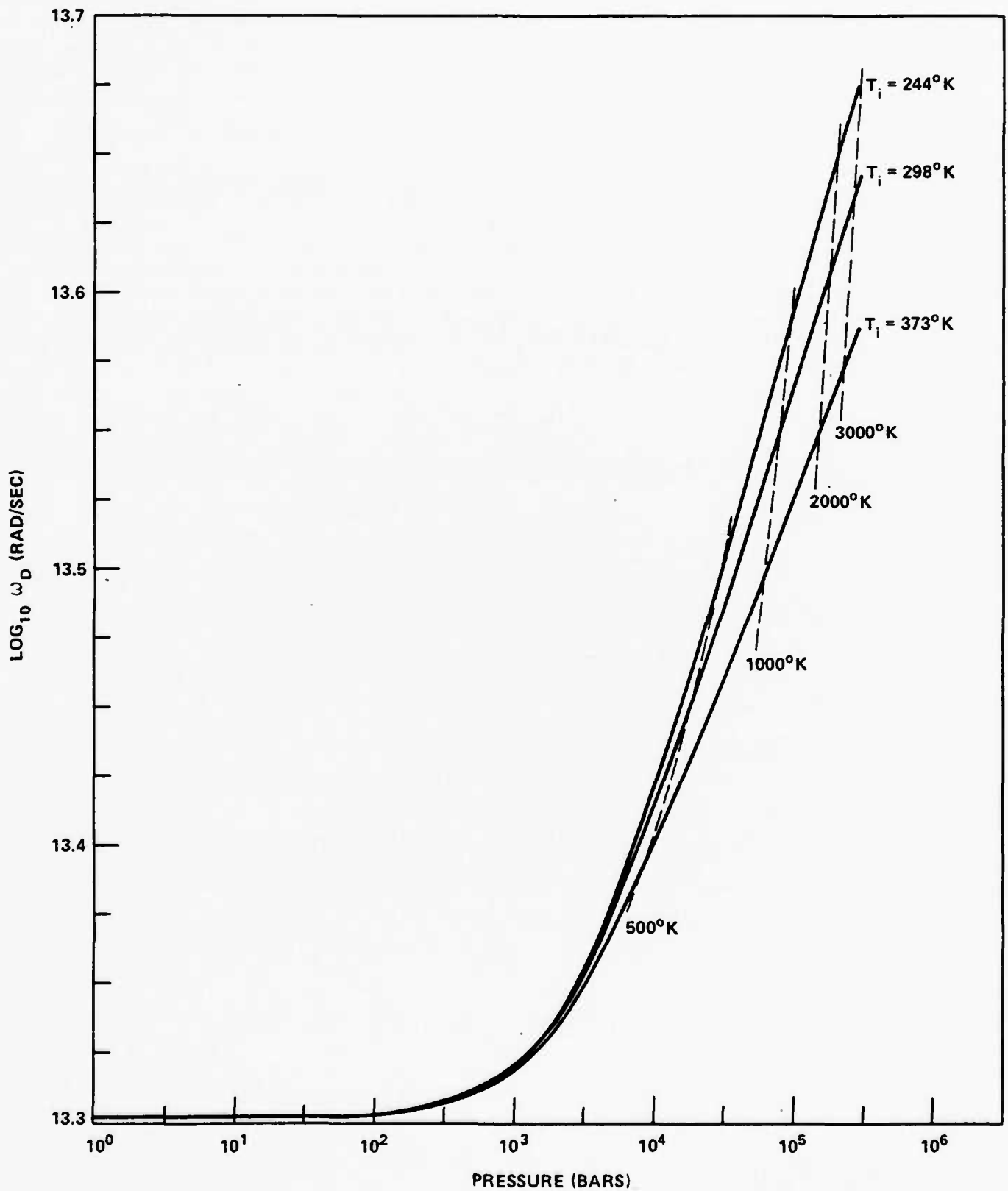


FIGURE 3. DATA SHOWN IN FIGURE 2 , BUT ON A LOG-LOG SCALE

pressure for this mode is a sort of pressure-time criterion for initiation of reactions. For it is clear that a shock of a given pressure must be sustained for a time which is some multiple (of order unity) of W_0^{-1} in order for significant dissociation to occur.

COMPARISON WITH PRESSURE-TIME CRITICAL INITIATION DATA

In this regard, de Longueville, Fauquignon, and Moulard reported critical initiation data in the pressure-time plane for several condensed explosives including nitromethane.¹¹ We have included that data, shown as short dotted line segments labelled DLFM on the graphs in Figures 4 and 5. The inverse of de Longueville, Fauquignon, and Moulard's time is plotted on the ordinate, W_0^{-1} . It is interesting, though possibly coincidental, that the DLFM data, over its limited range, show times that are approximately six to seven times the NO_2 rocking (parallel) transition lifetimes at the corresponding pressures and the curve segments show roughly the same slope.

¹¹de Longueville, Y., Fauquignon, C., and Moulard, H., Initiation of Several Condensed Explosives by a Given Duration Shock Wave, Sixth Symposium (International) on Detonation, ONR ACR-221, Aug 1976, pp. 105 ff.

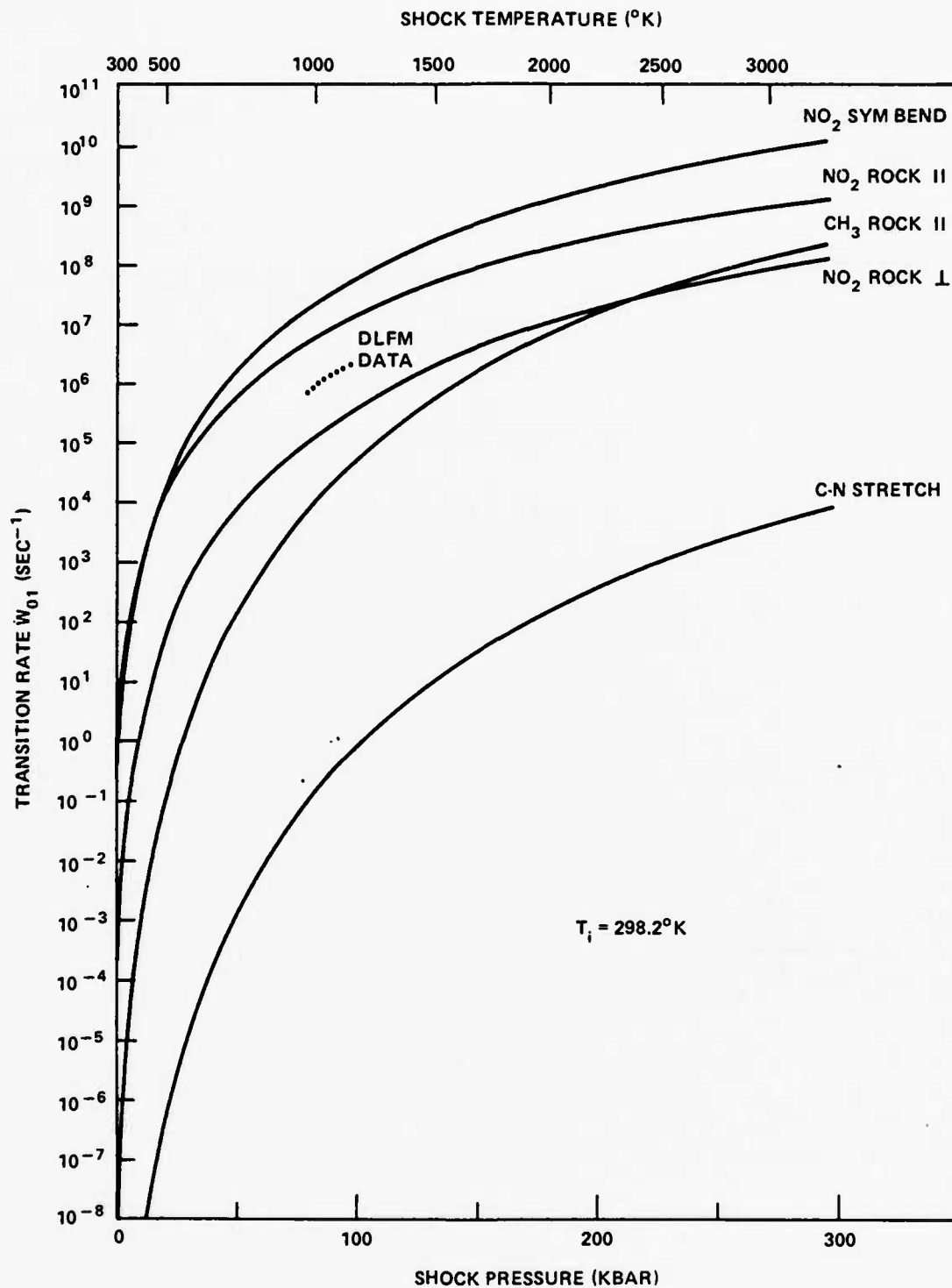


FIGURE 4. NON-RADIATIVE (SHOCK-INDUCED) TRANSITION RATES FOR SEVERAL INTERNAL MODES OF NITROMETHANE PLOTTED AS A FUNCTION OF SHOCK PRESSURE ALONG THE HUGONIOT WITH INITIAL TEMPERATURE 298.2°K

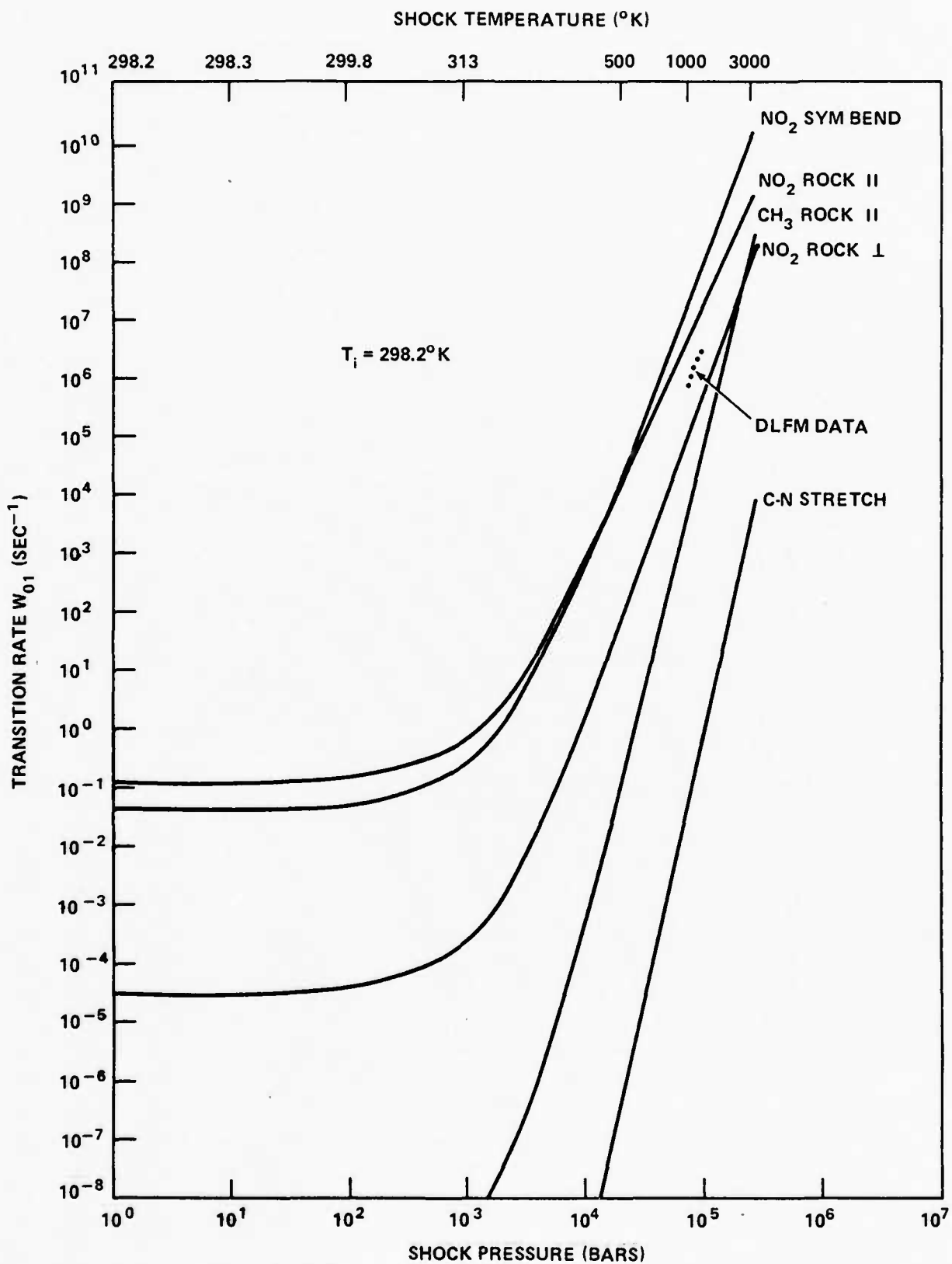


FIGURE 5. DATA OF FIGURE 4, BUT ON A LOG-LOG SCALE

CHAPTER 6

CONCLUSION

We have presented a quantum mechanical calculation of the transition rates for shock induced transitions between the low lying internal molecular normal modes in a molecular solid. We have assumed that the shock produces a distribution of acoustic phonons which becomes thermalized before any significant internal mode phonons are created. This assumption seems to have been justified in the case of nitromethane in which the shortest internal mode transition lifetimes are of the order of nanoseconds while lattice relaxation times determined from Van Vleck's calculation are of the order of picoseconds or less. In particular, at the von Neumann spike pressure in nitromethane (about 200 kbar), the NO_2 rocking (parallel to NO_2 plane) mode has an excitation time of about 4 nsec.

When we compared the excitation lifetimes with the pressure-time critical initiation data of de Longueville, Fauquignon, and Moulard, we found that the times were not inconsistent with the hypothesis that the overall dissociation rate limiting factor is the relaxation time (ω_0^{-1}) for transferring energy from the acoustic modes to a limited number of internal molecular modes (NO_2 rocking parallel to NO_2 plane to nitromethane).

We must reiterate, however, that the numbers we have obtained for nitromethane are subject to many uncertainties, among them, uncertainties in determining the Huang-Rhys factor S_0 for each mode and the uncertainty in a suitable choice of Debye frequency ω_D . Small changes in both of these quantities lead to large changes in the transition rates. Also, for the great majority of modes which are not optically active, it is not possible to determine S_0 . Perhaps the results of neutron scattering experiments may give useful information on these modes. Other problems are the question of the validity of the Condon approximation [Equation (9)], the determination of the anharmonic coupling coefficients [Equation (30) and (31)], the validity of isolating one internal mode, neglecting the interaction between internal modes, and the use of a single frequency ω_D to characterize the acoustic spectrum. Finally, the shock data available for nitromethane is for the liquid state, whereas, the calculations, strictly speaking, apply to the solid state. We hope that experimenters will be encouraged to undertake shock experiments on solid nitromethane in order to obtain both Hugoniot data and critical initiation data. In order to apply the results presented here to other solid explosives it is necessary that the explosive be homogeneous and have an internal mode spectrum clearly distinguished and well separated from the lattice spectrum.

REFERENCES

1. Pastine, D. J., Edwards, D. J., Jones, H. D., Richmond, C. T., and Kim, K., "Some New Concepts Relating to the Initiation and Failure of Detonable Explosives," in High Pressure Science and Technology, Vol. 2, ed by K. D. Timmerhaus and M. S. Barber, Plenum, New York, 1979.
2. Van Vleck, J. H., "Calculation of Energy Exchange between Lattice Oscillators," Physical Review, 59, 730 (1941).
3. Perlin, Yu. E., "Modern Methods in the Theory of Many-Phonon Processes," Soviet Physics-Uspekhi, 6, 542 (1963).
4. Lin, S. H., "Theory of Vibrational Relaxation and Infrared Absorption in Condensed Media," J. Chem. Phys., 65, 1053 (1976).
5. Lax, M. J., J. Chem. Phys., 20, 1752 (1952).
6. Lin, S. H., "On the Master Equation Approach of Vibrational Relaxation in Condensed Media," J. Chem. Phys., 61, 3810 (1974).
7. Plendl, J. N., "New Spectral and Atomistic Relations in Physics and Chemistry of Solids," in Optical Properties of Solids, ed. by S. Nudelman and S. S. Mitra, Plenum, New York (1969), p. 310 ff.
8. Huang, K. and Rhys, A., "Theory of Light Absorption and Non-Radiative Transitions in F-Centers," Proc. Roy. Soc., A204, 406 (1950).
9. Born, M. and Huang, K., Dynamical Theory of Crystal Lattices, (Oxford Univ. Press, 1954), sec. 4.
10. Hardesty, D. R. and Lysne, P. C., Shock Initiation and Deformation Properties of Homogeneous Explosives, Sandia Laboratories Report SLA 74-0165, May 1974.
11. de Longueville, Y., Fauquignon, C., and Moulard, H., Initiation of Several Condensed Explosives by a Given Duration Shock Wave, Sixth Symposium (International) on Detonation, ONR ACR-221, Aug 1976, pp. 105 ff.

APPENDIX A

BORN-OPPENHEIMER APPROXIMATION

Suppose we can split the coordinates of a system into two groups, a fast subsystem $\{r_i\}$ and a slow subsystem $\{q_k\}$. The Hamiltonian of the system is

$$H(r_i, q_k) = T_r + T_q + V(r_i, q_k) \quad (A-1)$$

where T_r and T_q are the kinetic energy operators for the fast and slow coordinates, respectively. Let

$$H_r(q_k) = T_r + V(r_i, q_k) \quad (A-2)$$

and consider the solutions ψ_s of the eigenvalue problem

$$H_r \psi_s(r_i, q_k) = \epsilon_s(q_k) \psi_s(r_i, q_k) \quad (A-3)$$

The eigenvalues ϵ_s and the wave functions $\psi_s(r_i)$ depend parametrically on the coordinates q_k . Suppose the set $\{\psi_s(r_i, q_k)\}$ is a complete orthonormal set in r -space for every of values of q_k . Then any solution Ψ of the original system Schrödinger equation,

$$H\Psi = E\Psi \quad (A-4)$$

can be written

$$\Psi(r_i, q_k) = \sum_s \phi_s(q_k) \psi_s(r_i, q_k) \quad (A-5)$$

Then Equation (A-4) is equivalent to

$$\sum_s [\epsilon_s(q_k) + T_q - E] \phi_s(q_k) \psi_s(r_i, q_k) = 0 \quad (A-6)$$

Now, consider T_q and $\psi_s(r_i, q_k)$ as operators in q -space. Then

$$T_q \psi_s(r_i, q_k) = [T_q, \psi_s(r_i, q_k)] + \psi_s(r_i, q_k) T_q \quad (A-7)$$

Substituting (A-7) into (A-6) we obtain the following equivalent version of (A-4):

$$(\mathcal{H} + \mathcal{L}) \Psi = E\Psi \quad (A-8)$$

where

$$\mathcal{H}\Psi = \sum_s \psi_s(r_i, q_k) \left\{ T_q + \epsilon_s(q_k) \right\} \phi_s(q_k) \quad (\text{A-9a})$$

$$\mathcal{L}\Psi = \sum_s [T_q, \psi_s(r_i, q_k)] \phi_s(q_k) \quad (\text{A-9b})$$

In Equations (A-9a,b), \mathcal{H} is the adiabatic Hamiltonian and \mathcal{L} is the non-adiabatic operator. The usual Born-Oppenheimer basis is obtained by ignoring \mathcal{L} and solving the equation $\mathcal{H}\Psi = E\Psi$, or, equivalently,

$$\left\{ T_q + \epsilon_s(q_k) \right\} \phi_{sn}(q_k) = E_{sn} \phi_{sn}(q_k) \quad (\text{A-10})$$

where s, n are the fast and slow subsystem quantum numbers, respectively. The Born-Oppenheimer basis states are

$$\Psi_{sn}(r_i, q_k) = \psi_s(r_i, q_k) \phi_{sn}(q_k) \quad (\text{A-11})$$

APPENDIX B

NON-ADIABATIC OPERATOR

Equation (A-9b) defines the non-adiabatic operator. What does this operator look like if the slow subsystem consists of a set of harmonic oscillators? In this case the kinetic energy operator T_q is

$$T_q = \sum_{\kappa} T_{q\kappa} = -\frac{1}{2} \sum_{\kappa} \hbar \omega_{\kappa} \frac{\partial^2}{\partial q_{\kappa}^2} \quad (\text{B-1})$$

In Equation (B-1), the kinetic energy has been written using dimensionless coordinates $q = \sqrt{m\omega/\hbar} x$ and the normal mode frequencies are denoted by ω_{κ} . The action of the non-adiabatic operator on Ψ_{sn} is therefore

$$\mathcal{L}\Psi_{sn} = - \sum_{\kappa} \hbar \omega_{\kappa} \left\{ \frac{\partial \psi_s}{\partial q_{\kappa}} \frac{\partial \phi_{sn}}{\partial q_{\kappa}} + \frac{1}{2} \frac{\partial^2 \psi_s}{\partial q_{\kappa}^2} \phi_{sn} \right\} \quad (\text{B-2})$$

APPENDIX C

EVALUATION OF SUM OVER STATES

Introducing the integral representation of the delta function, Equation (4) becomes

$$W(i \rightarrow f) = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} \sum_{m,n} \exp \{i(E_{fm} - E_{in})t/\hbar\} P_n |\langle fm | \mathcal{L} | in \rangle|^2 dt \quad (C-1)$$

In the lowest order, the acoustic mode wave functions are products of harmonic oscillator wave functions:

$$\phi_{in} = \prod_{\kappa} \phi_{in_{\kappa}}^{(\kappa)} \quad (C-2)$$

The energy levels are

$$E_{in} = E_i + \sum_{\kappa} \left(n_{\kappa} + \frac{1}{2} \right) \hbar \omega_{\kappa} \quad (C-3)$$

and the square of the matrix element appearing in (C-1) is

$$\begin{aligned} |\langle fm | \mathcal{L} | in \rangle|^2 &= \sum_{\kappa} |\mathcal{L}_{\kappa fi}|^2 \left| \langle \phi_{fn_{\kappa}}^{(\kappa)} | \frac{\partial \phi_{in_{\kappa}}^{(\kappa)}}{\partial q_{\kappa}} \rangle \right|^2 \prod_{\mu \neq \kappa} \left| \langle \phi_{fm_{\mu}}^{(\mu)} | \phi_{in_{\mu}}^{(\mu)} \rangle \right|^2 \\ &+ \sum_{\substack{\kappa, \lambda \\ \kappa \neq \lambda}} \mathcal{L}_{\kappa fi} \mathcal{L}_{\lambda fi}^* \langle \phi_{fn_{\kappa}}^{(\kappa)} | \frac{\partial \phi_{in_{\kappa}}^{(\kappa)}}{\partial q_{\kappa}} \rangle \langle \phi_{fn_{\lambda}}^{(\lambda)} | \frac{\partial \phi_{in_{\lambda}}^{(\lambda)}}{\partial q_{\lambda}} \rangle \prod_{\mu \neq \kappa} \langle \phi_{fm_{\mu}}^{(\mu)} | \phi_{in_{\mu}}^{(\mu)} \rangle \prod_{\nu \neq \lambda} \langle \phi_{fm_{\nu}}^{(\nu)} | \phi_{in_{\nu}}^{(\nu)} \rangle \\ &+ \left(\sum_{\lambda} m_{\lambda fi} \right)^* \sum_{\kappa} \mathcal{L}_{\kappa fi} \langle \phi_{fn_{\kappa}}^{(\kappa)} | \frac{\partial \phi_{in_{\kappa}}^{(\kappa)}}{\partial q_{\kappa}} \rangle \langle \phi_{fn_{\kappa}}^{(\kappa)} | \phi_{in_{\kappa}}^{(\kappa)} \rangle^* \prod_{\mu = \kappa} \left| \langle \phi_{fm_{\mu}}^{(\mu)} | \phi_{in_{\mu}}^{(\mu)} \rangle \right|^2 + c.c. \end{aligned}$$

$$+ \left| \sum_{\kappa} m_{\kappa fi} \right|^2 \prod_{\mu} \left| \langle \phi_{fm}^{(\mu)} | \phi_{in}^{(\mu)} \rangle \right|^2 \quad (C-4)$$

Substituting (C-4) in (C-1) we obtain

$$W(i \rightarrow f) = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} \exp(i\omega_{fi}t) \left\{ \tilde{F}_{fi}(t) + \tilde{E}_{fi}(t) + \tilde{H}_{fi}(t) + \tilde{M}_{fi}(t) \right\} dt \quad (C-5)$$

where

$$\omega_{fi} = (E_f - E_i)/\hbar \quad (C-5a)$$

$$\tilde{F}_{fi}(t) = \sum_{\kappa} |L_{\kappa fi}|^2 \tilde{F}_{\kappa fi}(t) \prod_{\mu \neq \kappa} G_{\mu fi}(t) \quad (C-5b)$$

$$\tilde{E}_{fi}(t) = \sum_{\substack{\kappa, \lambda \\ \kappa \neq \lambda}} L_{\kappa fi} L_{\lambda fi}^* \tilde{E}_{\kappa fi}(t) \tilde{E}_{\lambda fi}^*(-t) \prod_{\substack{\mu \neq \kappa \\ \mu \neq \lambda}} G_{\mu fi}(t) \quad (C-5c)$$

$$\tilde{H}_{fi}(t) = \sum_{\kappa} L_{\kappa fi} \tilde{E}_{\kappa}(t) \prod_{\mu \neq \kappa} G_{\mu fi}(t) \sum_{\lambda} m_{\lambda fi}^* + \text{complex conjugate} \quad (C-5d)$$

$$\tilde{M}_{fi}(t) = \left| \sum_{\kappa} m_{\kappa fi} \right|^2 \prod_{\mu} G_{\mu fi}(t) \quad (C-5e)$$

and

$$G_{\mu fi}(t) = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} P_n e^{i(m-n)\omega_{\mu}t} \left| \langle \phi_{fm}^{(\mu)} | \phi_{in}^{(\mu)} \rangle \right|^2 \quad (C-6a)$$

$$\tilde{F}_{\kappa fi}(t) = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} P_n e^{i(m-n)\omega_{\kappa}t} \left| \langle \phi_{fm}^{(\kappa)} | \frac{\partial}{\partial q_{\kappa}} \phi_{in}^{(\kappa)} \rangle \right|^2 \quad (C-6b)$$

$$\tilde{E}_{kfi}(t) = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} P_n e^{i(m-n)\omega_k t} \langle \phi_{fm}^{(\kappa)} | \frac{\partial}{\partial q_k} \phi_{in}^{(\kappa)} \rangle \langle \phi_{fm}^{(\kappa)} | \phi_{in}^{(\kappa)} \rangle \quad (C-6c)$$

The sums in Equations (C-6a,b,c) can be evaluated using the expression for the density matrix of the harmonic oscillator in the coordinate representation (Slater's sum or Mehler's formula).^{C-1} The results are

$$G_{kfi}(t) = \exp \left\{ E_k(t) \Delta_{kfi}^2 \right\} \quad (C-7a)$$

$$\tilde{F}_{kfi}(t) = F_k(t) + \left[E_k(t) \Delta_{kfi} \right]^2 \quad (C-7b)$$

$$\tilde{E}_{kfi}(t) = E_k(t) \Delta_{kfi} G_k(t) \quad (C-7c)$$

where

$$F_k(t) = \frac{\cosh(i\omega_k t + \frac{1}{2} \beta \hbar \omega_k)}{2 \sinh(\frac{1}{2} \beta \hbar \omega_k)} \quad (C-8a)$$

$$E_k(t) = F_k(t) - \frac{1}{2} \coth \left(\frac{1}{2} \beta \hbar \omega_k \right) \quad (C-8b)$$

$$\Delta_{kfi} = q_{kf} - q_{ki} \quad (C-8c)$$

In Equation (C-8c), q_{kf} and q_{ki} are the equilibrium values of the acoustic coordinates when the fast subsystem is in states f and i , respectively. Using the results above, we can write the expression for the transition rate as follows:

$$W(i \rightarrow f) = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} \exp(i\omega_{fi}t) F_{fi}(t) G_{fi}(t) dt \quad (C-9)$$

where

$$\begin{aligned} F_{fi}(t) = & \sum_{\kappa} |\mathcal{L}_{\kappa fi}|^2 F_{\kappa}(t) + \sum_{\kappa} \mathcal{L}_{\kappa fi} \Delta_{\kappa fi} E_{\kappa}(t) \sum_{\lambda} \mathcal{L}_{\lambda fi}^* \Delta_{\lambda fi} E_{\lambda}(t) \\ & + M_{fi}^* \sum_{\kappa} \mathcal{L}_{\kappa fi} \Delta_{\kappa fi} E_{\kappa}(t) + M_{fi} \sum_{\kappa} \mathcal{L}_{\kappa fi}^* \Delta_{\kappa fi} E_{\kappa}(t) \end{aligned}$$

^{C-1}See, for example, O'Rourke, R. C., Phys. Rev., 91, 265 (1953).

$$+ |M_{fi}|^2 \quad (C-9a)$$

$$M_{fi} = \sum_{\kappa} m_{\kappa fi} \quad (C-9b)$$

$$G_{fi}(t) = \exp \left\{ \sum_{\kappa} F_{\kappa}(t) \Delta_{\kappa fi}^2 - S \right\} \quad (C-9c)$$

$$S = \sum_{\kappa} \frac{1}{2} \coth \left(\frac{1}{2} \beta \hbar \omega_{\kappa} \right) \Delta_{\kappa fi}^2 \quad (C-9d)$$

APPENDIX D

SADDLE POINT INTEGRAL FOR TRANSITION RATE

It is convenient to make the change of variable $z = it$ in the expression for $W(i+f)$ in Equation (9). Then Equation (10) can be written in the form

$$W(i+f) = \frac{1}{i\hbar^2} \int_{-i\infty}^{i\infty} F_{fi}(-iz) e^{g(z)} dz \quad (D-1)$$

where

$$g(z) = \omega_{fi} z + \sum_{\kappa} \frac{\cosh(\omega_{\kappa} z + \frac{1}{2} \beta \hbar \omega_{\kappa})}{2 \sinh(\frac{1}{2} \beta \hbar \omega_{\kappa})} \Delta_{\kappa fi}^2 - S \quad (D-2)$$

At a saddle point, $g'(z_0) = 0$ so that

$$\omega_{fi} + \sum_{\kappa} \omega_{\kappa} \frac{\sinh(\omega_{\kappa} z + \frac{1}{2} \beta \hbar \omega_{\kappa})}{2 \sinh(\frac{1}{2} \beta \hbar \omega_{\kappa})} \Delta_{\kappa fi}^2 = 0 \quad (D-3)$$

Equation (D-3) has many complex roots but precisely one real root. There is at least one real root since the hyperbolic sine function goes to $\pm\infty$ when $z \rightarrow \pm\infty$. There cannot be more than one real root because $g''(z)$ is never zero for real z implying that $g(z)$ is monotonic [See Equation (D-4)].

$$g''(z) = \sum_{\kappa} \omega_{\kappa} \frac{2 \cosh(\omega_{\kappa} z + \frac{1}{2} \beta \hbar \omega_{\kappa})}{2 \sinh(\frac{1}{2} \beta \hbar \omega_{\kappa})} \Delta_{\kappa fi}^2 \quad (D-4)$$

In particular, $g''(z_0) > 0$ so the direction of steepest descent is along the imaginary axis. Near the saddle point

$$g(z) \approx g(z_0) + \frac{1}{2} (z - z_0)^2 g''(z_0) \quad (D-5)$$

Thus, deforming the contour of integration to pass through the saddle point, we get

$$W(i+f) = \frac{1}{\hbar^2} F_{fi}(-iz_0) \exp \{g(z_0)\} \int_{-\infty}^{\infty} \exp \left\{ -\frac{1}{2} t^2 g''(z_0) \right\} dt \quad (D-6)$$

and the final result is

$$W(i+f) = \frac{1}{\hbar^2} \sqrt{\frac{2\pi}{g''(z_0)}} F_{fi}(-iz_0) \exp \{g(z_0)\} \quad (D-7)$$

More details on the saddle point integral may be found in Perlin's review article (Reference 3, footnote, p. 3).

If we can replace the acoustic frequencies ω_k by a single average frequency ω_D , a considerable simplification is achieved. Then

$$\begin{aligned} F_{fi}(-iz_0) = & \sum_k |\mathcal{L}_{kfi}|^2 F_D + \left| \sum_k \mathcal{L}_{kfi} \Delta_{kfi} \right|^2 \left\{ F_D - \frac{1}{2} \coth \left(\frac{1}{2} \beta \hbar \omega_D \right) \right\}^2 \\ & + \left\{ \sum_{\lambda} m_{\lambda fi}^* \sum_k \mathcal{L}_{kfi} \Delta_{kfi} + \sum_{\lambda} m_{\lambda fi} \sum_k \mathcal{L}_{kfi}^* (\Delta_{kfi}) \right\} \left[F_D - \frac{1}{2} \coth \left(\frac{1}{2} \beta \hbar \omega_D \right) \right] \\ & + \left| \sum_k m_{kfi} \right|^2 \end{aligned} \quad (D-8)$$

where

$$F_D = \frac{\cosh(\omega_D z_0 + \frac{1}{2} \beta \hbar \omega_D)}{2 \sinh(\frac{1}{2} \beta \hbar \omega_D)} \quad (D-8a)$$

Equation (D-3) which determines z_0 becomes

$$p = x \sinh \left(\omega_D z_0 + \frac{1}{2} \beta \hbar \omega_D \right) \quad (D-9)$$

where

$$p = - \frac{\omega_{fi}}{\omega_D} \quad (D-9a)$$

$$x = \frac{S_o}{\sinh(\frac{1}{2} \beta \hbar \omega_D)} \quad (D-9b)$$

$$S_o = \frac{1}{2} \sum_{\kappa} \Delta_{\kappa fi}^2 \quad (D-9c)$$

The solution is

$$\omega_{fi} z_o = \frac{1}{2} \beta \hbar \omega_D p + |p| \ln \left\{ \frac{x}{|p| + 2S_o F_D} \right\} \quad (D-10)$$

and

$$F_D = \frac{\sqrt{x^2 + p^2}}{2S_o} \quad (D-10a)$$

Also,

$$\exp\{g(z_o)\} = \exp\left\{\frac{1}{2} \beta \hbar \omega_D p + 2S_o F_D - S\right\} \left\{ \frac{x}{|p| + 2S_o F_D} \right\}^{|p|} \quad (D-11a)$$

$$g''(z_o) = 2\omega_D^2 S_o F_D \quad (D-11b)$$

APPENDIX E

EVALUATION OF \mathcal{L}_{kfi} AND m_{kfi}

Using the result in Equation (26) we obtain

$$\left(\psi_f, \frac{\partial \psi_i}{\partial q_k} \right) = \int \sqrt{\rho} \psi_f^{(HO)}(Z) \frac{\partial}{\partial q_k} \left\{ \sqrt{\rho} \psi_i^{(HO)}(Z) \right\} dq_0 \quad (E-1)$$

and, transforming the variable of integration from q_0 to Z , the result is

$$\left(\psi_f, \frac{\partial \psi_i}{\partial q_k} \right) = \int \psi_f^{(HO)}(Z) \frac{d\psi_i^{(HO)}(Z)}{dZ} \frac{\partial Z}{\partial q_k} dZ + \frac{\partial}{\partial q_k} \left(\ln \sqrt{\rho} \right) \delta_{fi} \quad (E-2)$$

Since $f \neq i$, the second term in Equation (E-2) is zero. Differentiating Equation (23) we obtain

$$\hbar \omega_0 \frac{\partial Z}{\partial q_k} = \frac{1}{2} \rho^{-4} C_k Z + 2\rho^{-3} \sum_{\lambda} B_{k\lambda} q_{\lambda} - 2\rho^{-7} B C_k \quad (E-3)$$

Using Equations (E-3), (E-2), and (7a) we obtain

$$\begin{aligned} \mathcal{L}_{kfi} = & - \frac{\hbar \omega_k}{\hbar \omega_0} \left\{ \frac{1}{2} \rho^{-4} C_k \langle f | Z \frac{\partial}{\partial Z} | i \rangle \right. \\ & \left. + 2 \left(\rho^{-3} \sum_{\lambda} B_{k\lambda} q_{\lambda} - \rho^{-7} B C_k \right) \langle f | \frac{\partial}{\partial Z} | i \rangle \right\} \quad (E-4) \end{aligned}$$

where $\langle f | Z \frac{\partial}{\partial Z} | i \rangle$ and $\langle f | \frac{\partial}{\partial Z} | i \rangle$ are the usual harmonic oscillator matrix elements. These may be evaluated most conveniently by writing Z and $\partial/\partial Z$ in terms of the creation and annihilation operators, a^+ and a , and then using the raising and lowering properties of these operators.

$$Z = \frac{1}{\sqrt{2}} (a + a^+) \quad (E-5a)$$

$$\frac{\partial}{\partial Z} = \frac{1}{\sqrt{2}} (a - a^+) \quad (E-5b)$$

$$a^+ |n\rangle = \sqrt{n+1} |n+1\rangle \quad (\text{E-5c})$$

$$a |n\rangle = \sqrt{n} |n-1\rangle \quad (\text{E-5d})$$

The end result is

$$\begin{aligned} \mathcal{L}_{\kappa fi} = & -\frac{\hbar\omega_{\kappa}}{\hbar\omega_0} \left\{ \sqrt{2} \left[\rho^{-3} \sum_{\lambda} B_{\kappa\lambda} q_{\lambda} - \rho^{-7} B C_{\kappa} \right] \left[\sqrt{i} \delta_{f,i-1} - \sqrt{i+1} \delta_{f,i+1} \right] \right. \\ & \left. + \frac{1}{4} \rho^{-4} C_{\kappa} \left[\sqrt{i(i-1)} \delta_{f,i-2} - \delta_{fi} - \sqrt{(i+1)(i+2)} \delta_{f,i+2} \right] \right\} \quad (\text{E-6}) \end{aligned}$$

A similar, though lengthier, calculation yields $\mathcal{M}_{\kappa fi}$. Since the result has many terms, we give here only the lowest order term involving powers and products of C_{κ} and $B_{\kappa\lambda}$:

$$\mathcal{M}_{\kappa fi} = -\sqrt{2} \hbar\omega_{\kappa} \frac{B_{\kappa\kappa}}{\hbar\omega_0} \left(\sqrt{i} \delta_{f,i-1} - \sqrt{i+1} \delta_{f,i+1} \right) \quad (\text{E-7})$$

APPENDIX F

ACOUSTIC MODE WAVE EQUATION APPROXIMATE SOLUTIONS

The internal mode eigenvalues, Equation (25), are the effective potentials which determine the acoustic mode Born-Oppenheimer wave functions via Equation (22). To obtain an approximate solution, expand the eigenvalues ϵ_f in powers of q_k up to quadratic terms. This is a good approximation if the anharmonic corrections to the total Hamiltonian are small so that $B, C \ll 1$. Then,

$$\frac{\partial \epsilon_s}{\partial q_k} \approx (s + \frac{1}{2}) C_k + \hbar \omega_k q_k \quad (F-1)$$

and

$$\frac{\partial^2 \epsilon_s}{\partial q_k \partial q_\lambda} \approx \hbar \omega_k \delta_{k\lambda} - (s + \frac{1}{2}) \frac{C_k C_\lambda}{\hbar \omega_0} \quad (F-2)$$

Thus, the equilibrium acoustic coordinates are

$$q_{ks} \approx - (s + \frac{1}{2}) \frac{C_k}{\hbar \omega_k} \quad (F-3)$$

and the effective potential is

$$\epsilon_s \approx \epsilon_s(q_{ks}) + \sum_k \frac{1}{2} \hbar \omega_k (q_k - q_{ks})^2 \quad (F-4)$$

In Equation (F-4) we have ignored the off-diagonal quadratic terms since they are small under our previous assumptions. These terms lead to mixing of the acoustic coordinates and subsequent modifications of the acoustic frequencies. In terms of the variables $\tilde{q}_k = q_k - q_{ks}$, the acoustic wave equation, Equation (22), becomes

$$\left\{ \sum_k \frac{1}{2} \hbar \omega_k \left(\tilde{q}_k^2 - \frac{\partial^2}{\partial \tilde{q}_k^2} \right) + J_s \right\} \phi_{sn} = E_{sn} \phi_{sn} \quad (F-5)$$

where

$$J_s = (s + \frac{1}{2})\hbar\omega_0 - \sum_{\kappa} \frac{1}{2} \hbar\omega_{\kappa} q_{\kappa}^2 \quad (F-6)$$

Thus the total energy eigenvalues are

$$E_{sn} = J_s + \sum_{\kappa} (n_{\kappa} + \frac{1}{2})\hbar\omega_{\kappa} \quad (F-7)$$

APPENDIX G

APPROXIMATE TRANSITION RATE FORMULA

We approximate the coefficients C_k and $B_{k\lambda}$ using Equations (30) and (31) as our guide:

$$C_k = \frac{f_1 \beta}{\sqrt{N} \sqrt{\omega_D} \omega_0} \left(\frac{\hbar}{M} \right)^{3/2} \quad (G-1)$$

$$B_{k\lambda} = \frac{f_2 \beta}{N \omega_D \sqrt{\omega_0}} \left(\frac{\hbar}{M} \right)^{3/2} \quad (G-2)$$

We have denoted $1/2 f''(r_e)$ by β . The quantities f_1 and f_2 are dimensionless numbers which we will later set to $1/\sqrt{2}$ and 2, respectively. Substitute Equation (27) into (9e) and substitute the result into Equation (11b) to obtain the Huang-Rhys factor for a transition from state i to state f :

$$S_0 = \frac{(f-i)^2}{2\hbar^2 \omega_D^2} \sum_k C_k^2 \quad (G-3)$$

The sum contains N terms, so upon substituting Equation (G-1) into (G-3) we get

$$S_0 = \frac{1}{2} f_1^2 (f-i)^2 \left(\frac{\beta}{M \omega_D^2} \right) \left(\frac{\hbar}{M \omega_0} \right) \frac{\omega_D}{\omega_0} \quad (G-4)$$

In the following, we set $f=i+1$. Using Equations (28), (9e), (27), (G-1), (G-2), and (G-4) we obtain

$$\left| \sum_k \mathcal{L}_{k,i+1,i} \Delta_k \right|^2 = 4 \left(\frac{f_2}{f_1} \right)^2 (i+1)(2i+1)^2 S_0^3 (\hbar \omega_D)^2 \frac{\omega_D}{\omega_0} \left\{ 1 + (2i+1) S_0 \omega_D / \omega_0 \right\} \quad (G-5)$$

The second term in curly brackets in Equation (G-5) arises from the second term in Equation (28). In our application, S_0 is much less than one, therefore, we can omit the second term in Equation (28). Similarly, we obtain

$$\sum_{\kappa} |\mathcal{L}_{\kappa, i+1, i}|^2 = 2 \left(\frac{f_2}{f_1} \right)^2 (i+1)(2i+1)^2 S_0^2 (\hbar\omega_D)^2 \omega_D/\omega_0 \quad (G-6)$$

$$2 \sum_{\kappa} m_{\kappa, i+1, i} \sum_{\lambda} \mathcal{L}_{\lambda, i+1, i} \Delta_{\lambda} = 8 \left(\frac{f_2}{f_1} \right)^2 (i+1)(2i+1) S_0^2 (\hbar\omega_D)^2 \omega_D/\omega_0 \quad (G-7)$$

$$\left| \sum_{\kappa} m_{\kappa, i+1, i} \right|^2 = 4 \left(\frac{f_2}{f_1} \right)^2 (i+1) S_0 (\hbar\omega_D)^2 \omega_D/\omega_0 \quad (G-8)$$

Substituting Equation (G-5)-(G-8) into Equation (D-8) we obtain

$$F_{i+1, i}(-iz_0) = \left(\frac{f_2}{f_1} \right)^2 (i+1)(\hbar\omega_D)^2 \frac{\omega_D}{\omega_0} S_0 \left\{ (2i+1)^2 [P+(P-S)^2] + 4(2i+1)(P-S) + 4 \right\} \quad (G-9)$$

where P and S are defined in Equations (10d) and (10e). If we now substitute Equation (G-9) into Equation (10), we obtain an expression for $W(i \rightarrow i+1)$ depending on T , ω_0 , ω_D , and S_0 . All the third order anharmonic coupling effects are condensed into the Huang-Rhys factor S_0 .

If $S_0 \ll 1$ and the temperature is not too large, we may simplify the result further. The upper temperature limitation is determined by the condition $x^2 \ll 1$ where x is defined in Equation (11c). Thus the condition is

$$\frac{1}{2} \beta \hbar \omega_D > \operatorname{arcsinh} S_0 = S_0 \quad (G-10)$$

Rearranging (G-10) we obtain the condition

$$T < T_D/2S_0 \quad (G-11)$$

where T_D is the Debye temperature. Under this condition, $S \ll 1$ and $P \approx |p|$. If we set $f_2 = 2$, $f_1 = 1/\sqrt{2}$, and $\Delta\Omega = \omega_D S_0/2$, we obtain the result given in Equations (2, 2a, 2b).

APPENDIX H

MOMENTS OF SPECTRAL BAND SHAPE FUNCTION

The r 'th moment of the distribution $I(\omega)$ is defined by

$$\langle \omega^r \rangle = \frac{\int_{-\infty}^{\infty} I(\omega) \omega^r d\omega}{\int_{-\infty}^{\infty} I(\omega) d\omega} \quad (\text{H-1})$$

where $I(\omega)$ is defined in Equation (34). In order to evaluate $\langle \omega^r \rangle$ note that

$$\int_{-\infty}^{\infty} \omega^r e^{-i\omega t} d\omega = 2\pi i^r \frac{d^r \delta(t)}{dt^r} \quad (\text{H-2})$$

where $\delta(t)$ is the Dirac delta function. Thus

$$\int_{-\infty}^{\infty} I(\omega) \omega^r d\omega = 2\pi i^r \int_{-\infty}^{\infty} e g(it) \frac{d^r \delta(t)}{dt^r} dt \quad (\text{H-3})$$

After r integrations by parts we obtain

$$\int_{-\infty}^{\infty} I(\omega) \omega^r d\omega = 2\pi \frac{d^r}{d(it)^r} \left[e g(it) \right]_{t=0} \quad (\text{H-4})$$

From Equation (D-2) we note that $g(0) = 0$ so that

$$\langle \omega^r \rangle = (\pm 1)^r \left. \frac{d^r e g(z)}{dz^r} \right|_{z=0} \quad (\text{H-5})$$

The positive sign is for absorption and the negative sign is for emission.

The average absorption or emission frequency is

$$\bar{\omega} = \langle \omega \rangle = \pm g'(0) = \pm (\omega_{fi} + \frac{1}{2} \Delta\Omega) \quad (\text{H-6})$$

where

$$\Delta\Omega = \sum_{\kappa} \omega_{\kappa} \Delta_{\kappa}^2 \quad (\text{H-7})$$

For absorption, let $\omega_o = \omega_{fi} > 0$ and for emission let $\omega_o = -\omega_{fi} > 0$. Then

$$\bar{\omega} = \omega_o \pm \frac{1}{2} \Delta\Omega \quad (\text{H-8})$$

Thus, the Stokes parameter $\Delta\Omega$ is the difference between the mean absorption and emission frequency. The second moment of the distribution is

$$\sigma^2 \equiv \langle (\omega - \bar{\omega})^2 \rangle = g''(0) = \frac{1}{2} \sum_{\kappa} \omega_{\kappa}^2 \coth \left(\frac{1}{2} \beta \hbar \omega_{\kappa} \right) \Delta_{\kappa}^2 \quad (\text{H-9})$$

and the third and fourth moments are

$$\langle (\omega - \bar{\omega})^3 \rangle = \pm g'''(0) = \pm \frac{1}{2} \sum_{\kappa} \omega_{\kappa}^3 \Delta_{\kappa}^2 \quad (\text{H-10})$$

$$\begin{aligned} \langle (\omega - \bar{\omega})^4 \rangle &= g^{(4)}(0) + 3[g''(0)]^2 \\ &= \frac{1}{2} \sum_{\kappa} \omega_{\kappa}^4 \coth \left(\frac{1}{2} \beta \hbar \omega_{\kappa} \right) \Delta_{\kappa}^2 + 3[g''(0)]^2 \end{aligned} \quad (\text{H-11})$$

Again, introducing an average acoustic frequency ω_D , we can express the moments in terms of the Huang-Rhys factor:

$$\Delta\Omega = 2S_o \omega_D \quad (\text{H-12})$$

$$\sigma^2 = \omega_D^2 S_o \coth \left(\frac{1}{2} \beta \hbar \omega_D \right) \quad (\text{H-13})$$

$$\gamma_3 \equiv \frac{\langle (\omega - \bar{\omega})^3 \rangle}{\sigma^3} = \left[S_o \coth \left(\frac{1}{2} \beta \hbar \omega_D \right) \right]^{-1} \quad (\text{H-14})$$

$$\gamma_4 \equiv \frac{\langle (\omega - \bar{\omega})^4 \rangle}{\sigma^4} - 3 = \left[S_o \coth \left(\frac{1}{2} \beta \hbar \omega_D \right) \right]^{-1} \quad (\text{H-15})$$

The skewness γ_3 and kurtosis γ_4 are measures of the deviation from a gaussian distribution.

APPENDIX I

DETERMINATION OF STOKES PARAMETER FROM BANDWIDTH

A straightforward method of obtaining a distribution with a finite number of specified moments would be to take the product of a polynomial with the error function, choosing the coefficients of the polynomial appropriately. An equivalent, but easier, approach is to take a linear combination of the error function and its derivatives with appropriate coefficients:

$$I(x) = \sum_{n=0}^{\infty} a_n \phi^{(n)}(x) \quad (I-1)$$

where

$$\phi(x) = \exp \left\{ -\frac{1}{2} x^2 \right\} / \sqrt{2\pi} \quad (I-2)$$

Integrating by parts we obtain the formulas

$$\int_{-\infty}^{\infty} x^{2r} I(x) dx = \frac{(2r)!}{2^r} \sum_{n=0}^r \frac{2^n a_{2n}}{(r-n)!} \quad (I-3)$$

$$\int_{-\infty}^{\infty} x^{2r+1} I(x) dx = -\frac{(2r+1)!}{2^r} \sum_{n=0}^r \frac{2^n a_{2n+1}}{(r-n)!} \quad (I-4)$$

If we wish $I(x)$ to be a normalized distribution with zero mean, unit standard deviation, skewness γ_3 , and excess γ_4 , then, from Equations (I-3) and (I-4) we find that $a_0 = 1$, $a_1 = 0$, $a_2 = 0$, $a_3 = -\gamma_3/6$, and $a_4 = \gamma_4/24$. Thus

$$I(x) = \phi(x) - \frac{\gamma_3}{3!} \phi^{(3)}(x) + \frac{\gamma_4}{4!} \phi^{(4)}(x) \quad (I-5)$$

Now let $x = (\omega - \bar{\omega})/\sigma$ and substitute for σ , γ_3 , and γ_4 from Equations (H-13), (H-14), and (H-15). If we then set $I(x) = I(0)/2$, we obtain an equation which can be solved numerically for S_0 , given $(\omega - \bar{\omega})/\omega_D$. Another distribution, quoted by Lax (Reference 5, footnote p. 4) as being due to Edgeworth, includes a sixth derivative

$$I(x) = \phi(x) = \frac{\gamma_3}{3!} \phi^{(3)}(x) + \frac{\gamma_4}{4!} \phi^{(4)}(x) + \frac{10\gamma_3^2}{6!} \phi^{(6)}(x) \quad (I-6)$$

The distribution (I-6) provides a not significantly better match for the higher moments.

APPENDIX J

VALIDITY OF THE SADDLE POINT APPROXIMATION

The saddle point approximation for the transition rate, outlined in Appendix D, is the first term in an asymptotic expansion in the sense defined by Poincare.^{J-1} In order for the first term to be a good approximation to the integral, the second term must be much smaller. The expansion for an integral of the form in Equation (D-1) has been worked out by Hoare for the case when the function $g(z)$ and its derivatives are of the order of N where N is the asymptotic expansion parameter and is presumed large.^{J-2} In our case, the relevant asymptotic parameter is p , defined in Equation (D-9a) in the average acoustic frequency approximation. The ratio of the second term in the asymptotic expansion to the first term must be much less than one. Using Hoare's result, we obtain

$$\frac{1}{8} \left| \frac{g^{(4)}(z_0)}{[g''(z_0)]^2} - \frac{5[g^{(3)}(z_0)]^2}{3[g''(z_0)]^3} \right| \ll 1 \quad (\text{J-1})$$

In the average acoustic frequency approximation, the derivatives of g are:

$$g^{(2n)}(z_0) = \omega_D^{2n} P ; n \geq 1 \quad (\text{J-2})$$

$$g^{(2n+1)}(z_0) = \omega_D^{2n+1} P ; n \geq 1 \quad (\text{J-3})$$

where $P = \sqrt{p^2 + x^2}$. Substituting (J-2) and (J-3) in (J-1), we get

$$\frac{1}{8p} \left| 1 - \frac{5}{3} \left(\frac{p}{P} \right)^2 \right| \ll 1 \quad (\text{J-4})$$

^{J-1}Jeffreys, H. and Jeffreys, B. S., Methods of Mathematical Physics, 3rd ed., Cambridge University Press, 1956, c. 17.

^{J-2}Hoare, M. R., J. Chem. Phys. 52, 5695 (1970).

From (J-4) we see that the second term in the expansion is less than $1/12$ the first term if $|p|$ is greater than one, independently of the value of x [$= S_0 / \sinh(\beta \hbar \omega_D / 2)$]. We also see that the second term is less than $1/8$ the first term if x is greater than one. In fact the expansion is asymptotic in the parameter P so that the approximation becomes better if either x or p becomes large.

In the case of non-radiative transitions, $|p| > 1$, so the criterion is satisfied whatever the value of S_0 . In fact $|p| \gg 1$ is required for the Born-Oppenheimer approximation to be valid.

For radiative transitions, however, the saddle point approximation is not good. For radiative transitions,

$$p = - (\omega_{fi} \pm \omega) / \omega_D \quad (J-5)$$

where the positive sign is for emission and the negative sign is for absorption at frequency ω . The range of values of p which are of interest (that is, values corresponding to frequencies within the spectral band) is then

$$p = S_0 \pm \frac{\Delta\omega}{2\omega_D} \quad (J-6)$$

where $\Delta\omega$ is the bandwidth. Since S_0 typically is much less than one, both $|p|$ and x will be much less than one so that condition (J-4) cannot be satisfied for values of p which correspond to frequencies lying within a spectral band.

DISTRIBUTION

	<u>Copies</u>		<u>Copies</u>
Chief of Naval Material		Superintendent	
Office of Naval Technology		Naval Post Graduate School	
Attn: MAT-07P (J. Enig)	1	Attn: Library	1
MAT-0712 (E. Zimet)	1	Monterey, CA 93940	
MAT-0716 (A. J. Faulstich)	1		
Washington, DC 20360		U. S. Army Research Office	
		Box CM	
Chief of Naval Research		Duke Station	
Attn: ONR-432 (R. Miller)	1	Durham, NC 27706	1
ONR-260 (D. Siegel)	1		
ONR-412 (B. Junker)	1	Air Force Office of Scientific	
800 N. Quincy Street		Research	
Arlington, VA 22217		Attn: Michael A. Strosio	15
		Bolling Air Force Base	
Commander		Washington, DC 20332	
Naval Sea Systems Command			
Attn: SEA-06R (D. J. Pastine)	1	Defense Technical Information	
SEA-62R (G. D. Edwards)	1	Center	
SEA-64E (R. Beauregard)	1	Cameron Station	
SEA-003	1	Alexandria, VA 22314	12
SEA-99612	1		
Washington, DC 20362		Library of Congress	
		Attn: Gift and Exchange	4
Commander		Washington, DC 20540	
Naval Research Laboratory			
Attn: J. Schnur	1	Director	
Washington, DC 20375		Los Alamos National Laboratory	
		Attn: J. Shaner	1
Commander		W. Fickett	1
Naval Weapons Center		W. Davis	1
Attn: T. L. Boggs	1	P. O. Box 1663	
R. Derr	1	Los Alamos, NM 87544	
Technical Library	1		
China Lake, CA 93555		Director	
		Livermore National Laboratory	
Superintendent		Attn: M. Finger	1
U.S. Naval Academy		E. Lee	1
Attn: Library	1	W. G. Von Holle	1
Annapolis, MD 21402		P. O. Box 808	
		Livermore, CA 94550	

DISTRIBUTION (Cont.)

	<u>Copies</u>		<u>Copies</u>
Director		R122	1
Sandia National Laboratory		R11 (H. Adolph)	1
Attn: D. Hayes	1	R12 (J. Short)	1
J. Kennedy	1	(M. Lutsky)	1
P. O. Box 5800		(J. Erkman)	1
Albuquerque, NM 87115		R13 (R. Bardo)	1
		(R. Bernecker)	1
New Mexico Institute of Mining		(A. R. Clairmont)	1
and Technology		(C. S. Coffey)	1
Attn: TERA	1	(N. Coleburn)	1
Socorro, NM 87801		(D. Demske)	1
		(C. Dickinson)	1
SRI International		(W. Elban)	1
333 Ravenswood Avenue		(J. Forbes)	1
Attn: M. Cowperthwaite	1	(H. Jones)	1
Menlo Park, CA 94025		(K. Kim)	1
		(E. Lemar)	1
Washington State University		(T. Liddiard)	1
Attn: Y. Gupta	1	(P. Miller)	1
G. Duvall	1	(C. Richmond)	1
Pullman, WA 99163		(H. Sandusky)	1
		(D. Tasker)	1
BDM Corporation		(J. Watt)	1
7915 Jones Branch Drive		(F. Zerilli)	20
Attn: E. T. Toton	1	R14	1
McLean, VA 22102		R15	1
		R16	1
Internal Distribution:		R34 (J. Sharma)	1
R04 (D. Love)	1	G35 (W. Mock)	1
R10 (D. Price)	1	(W. Holt)	1
(S. Jacobs)	1	E35	1
(T. Austin)	1	E431	9
R121	1	E432	3

END

FILMED

9-83

DTIC